

CHARACTERISTICS OF GROUNDWATER COLLOIDS ACROSS
AN AQUOD-UDULT TRANSITION IN FLORIDA FLATWOODS

By

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Chairman: Dr. Willie G. Harris
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Mobile colloids in soils and aquifers influence the natural geochemical fluxes, and may facilitate contaminant transport. Models predicting colloid movement have been tested experimentally for well defined systems. However, little is known about the nature of in-situ colloids in groundwater due to the difficulties in sampling and characterization. The overall goal of this study was to determine the extent to which concentration and composition of colloids suspended in groundwater are influenced by soil and hydrological properties on flatwoods, the most extensive landscape of Florida. The study site encompassed two soil suborders, Aquods and Udupts, and a narrow transition between them.

Monitoring data using multi-level piezometers verified a downward slope in the watertable across the soil transition from Aquod to Udupt. More rapid piezometric

response to rainfall events and slower piezometric head drop rate of the Aquod for periods in between rainfall events resulted in a consistently higher piezometric head for the Aquod argillic horizon than for the Uduto argillic horizon. Hence, discharge from the Aquod argillic horizon compensated for evapotranspiration and maintained wetter conditions in the upper sandy horizons.

The Aquod groundwater had significantly higher inorganic- and organic colloid concentrations than did the Uduto groundwater. It was also more acidic and had higher electrical conductivity. Significant decreases in total solids and organic C occurred with depth, with a particularly abrupt decrease in organic C within the spodic horizon of the Aquod. Colloids in groundwater were generally less than 1 μm in size for both soil areas, and predominantly less than 10 nm for the Aquod.

Quartz dominated the mineralogy of colloids in groundwater from all horizons, even though the readily-dispersible clay from argillic horizons was dominated by kaolinite and contained little quartz. No statistical correlation was found either between total colloid concentration in groundwater and soil dispersibility, or between organic C in groundwater and soil dispersible organic C. Also, the proportions of organic components to total solids in groundwater were significantly higher than those in soil matrices. These results lead to a conclusion that the composition of colloids in groundwater was not appreciably influenced by colloidal composition in the soil matrices from which the groundwater sample was collected. There are at least two possible explanations for this lack of correspondence: (1) entrainment of quartz released from upper sandy horizons, and (2) differential dispersion of quartz.

CHAPTER 1 INTRODUCTION

Soils are complex dispersive three-phase (solid, liquid, and gaseous) porous systems that occur in nature. Pore space between solids is typically occupied by aqueous solution under saturated condition such as groundwater or by both liquid and gas under unsaturated condition such as occurs in vadose zone. These phases are subject to transformation and redistribution resulting from biological and chemical influences. Examples of individual phase are quartz sand particles (solids) and air-filled pores (CO_2 , N_2 , O_2 , etc.). However, the liquid phase of soil generally contains a finite amount of very small solid particles suspended within them as well as dissolved salts. These small particles, commonly termed colloids (various definitions of *colloids* are discussed in Chapter 2), tend to remain dispersed within the liquid if they have a surface charge that promotes electrostatic repulsion. Colloids are, in effect, a mobile solid phase since they can move with water within soil. They also enhance the mobility of both natural and anthropogenic chemicals (e.g. metals and pesticides), and hence are important to the assessment of contaminant transport.

Recently, colloid-facilitated transport of low-solubility contaminants (such as Am, Ph, Pu, U, etc.) has been widely identified as an important mechanism of contaminant migration through subsurface environments. In field studies at hazardous waste sites, the

unexpectedly rapid transport of heavy metals, cationic radionuclides (e.g., Pu, Am, U, Ra, and Th) from some natural uranium deposits has been attributed to colloid-facilitated transport (Amrhein et al., 1993; Buddemeir and Hunt, 1988; Nelson and Orlandini, 1986; Penrose et al., 1990; Vilks et al., 1993). Some field studies have shown that the inorganic particles which enhance contaminant transport are composed of clay minerals, oxides, and carbonates ranging from 10 nm to a few micrometers ($1 \mu\text{m} = 1000 \text{ nm} = 10^{-6} \text{ m}$) in diameter. In most cases, these particles appear to be suspended in the subsurface systems by chemical and physical perturbations and to be potentially mobile. In addition, the role of organic colloids (or natural and synthetic organic macromolecules) in enhancing contaminant migration has been documented by laboratory and field studies. Laboratory studies have demonstrated that humic substances and microbial exudates can facilitate the transport of hydrophobic organic contaminants (HOCs) such as polycyclic aromatic hydrocarbons, polychlorinated biphenyls, and pesticides (Brusseau et al., 1994; Dohse and Lion, 1994; Dunnivant et al., 1992; Johnson and Amy, 1995; Liu and Amy, 1993), which are typically immobile due to strong binding to soil particles or low water solubility. Colloids thus play an important role in contaminant transport, groundwater management, and remediation efforts. However, little is known regarding the composition and concentration of colloids in aquifers and saturated groundwater zones of soils. Many models attempting to predict the colloid-facilitated transport of contaminants (Chung and Lee, 1992; Grindrod, 1993; Haber and Brenner, 1993; Jiang and Corapcioglu 1993; Liu and Amy, 1993; Mills et al., 1991; Smith and Degueldre, 1993) have also ignored the release and mobilization of colloids in porous subsurface systems.

Most natural porous media such as soils and other aquifer materials contain some colloids that are either attached to the surfaces of larger fixed particles or occur in a flocculated state (McCarthy and Zachara, 1989). The mass fraction of such colloids can vary from several ppm to several percent (Filella and Buffle, 1993). Colloids in natural porous media are usually immobile under normal water flow and geochemical conditions. However, if the electrostatic repulsion between particles is increased either by changing solution chemistry such as increasing pH and lowering ionic strength, they may be released into aqueous phase and be transported through the porous media. Estimation of the potential for colloid-facilitated transport should be based upon reliable characterization of colloids, which has received little attention because of sampling and analytical difficulties. There are few data available on colloid abundance and composition under field conditions, or on the extent to which soil morphological and hydrological factors influence these variables.

Effective prediction of environmental hazards due to toxic chemicals requires understanding of the pedological and hydrological conditions governing the mobilization of colloids and the extent to which colloids promote the migration of contaminants through the regolith to the groundwater system.

This research generated background data on colloids in shallow-groundwater from a common coastal plain landscape (flatwoods; see Chapter 3) by using special groundwater sampling techniques, and tested the following hypotheses pertaining to prospective transport of these colloids:

1. Colloids entrained in the pore water of flatwoods soils are subject to movement with the water;

2. Composition of colloids entrained in groundwater does not necessarily reflect that of the readily-dispersible clay in local soil matrix at the sampling point because the colloids are in transit;

3. The organic C fraction of the total solids in groundwater exceeds that of the readily-dispersible components from the soil matrix at the sampling point because C is likely transmitted continually from the surface.

The overall goal of this research was to determine the extent to which concentration and composition of colloids in groundwater were influenced by the groundwater dynamics and the nature of the soil matrix across an Aquod-Udult transition in Florida flatwoods landscape. Specific objectives of the study were:

1. To implement a minimally-intrusive technique for groundwater sampling that does not artificially mobilize colloids by mechanical disturbance or enhanced water flow velocity;

2. To determine the concentration, composition, and size distribution of colloids in groundwater sampled from various depths and horizons for selected flatwoods landscape systems;

3. To compare characteristics of the groundwater colloids to those of readily-dispersible colloids in the soil matrix from which water is sampled;

4. To evaluate the relation between organic C content in the aqueous phase and: (1) sampling depth, (2) soil colloid content, and (3) soil C content.

CHAPTER 2 LITERATURE REVIEW

Characterization of Colloids

Definition of *Colloid*

There are two different categories of definition for the term “colloid.” The first category consists of definitions in which a colloid is a bi- or multi-phase system in which one or more phases are suspended in finely-divided form (e.g., very small particles) within a continuous phase such as a liquid. An example of such a definition is that given in the American Heritage Dictionary (1995): “the colloid is a suspension of finely divided particles in a continuous medium in which the particles are approximately 5 to 5,000 Å in size, do not settle out of the substance rapidly, and are not readily filtered.” The second category includes definitions that refer to a colloid as a particle of a size that falls within a dimensional range. An example of the latter category of definition can be found in the *Glossary of Soil Science Terms 1996* (Soil Science Society of America, 1997): “*colloid* is a particle, which may be a molecular aggregate, with a diameter of 1 to 1000 nm. Soil clays and soil organic matter are often called soil colloids because they have particle sizes that are within, or approach colloidal dimensions.” Definitions of the first category

specify the condition of stability in suspension, including the case of liquid in liquid, but those of the second category do not. However, there is generally at least a tacit understanding that very small particles specified in the second category are within size ranges that are most readily suspended in aqueous media. The concept of colloid *stability* refers to the tendency for particles (or emulsion droplets) to remain suspended, and is only applied in a direct sense to colloids as systems, e.g., as defined under the first category. However, stable colloids, as systems, would be equivalent to stable suspensions of colloids, as particles. The term *colloid*, as used in this dissertation, is based on the particle dimension definition in the Glossary of Soil Science Terms, unless otherwise specified.

Dimensions of Colloids

The dimensional range that defines colloid in terms of particle size is arbitrary, and hence should be based on consensus within the scientific community. The range from 1 nm to 1 μm has been proposed (Everett, 1972; Buddemeier and Hunt, 1988) due to small influences of gravitational forces compared to the influences of Brownian motion for suspended particles within this size range. However, there is some disagreement as to the appropriate range of colloid dimensions. Harnish et al. (1994) defined colloids as ranging from 1 nm to 5 μm in diameter, whereas Stumm (1977) and Stumm and Morgan (1981) regarded colloids as particles having diameters less than 10 μm . Puls and Powell (1992) verified by borescope observations at several field sites that particles up to 1 μm

in size tend to remain suspended in water, and can be transported by groundwater (Kearl et al., 1994). However, Filella and Buffle (1993) claimed that smaller-sized colloids may play a more important role in colloid-facilitated contaminant transport due to their larger specific surface areas and mobility, and referred to the particulates ranging from 1 μm to 1 nm as submicro-colloids. Because particles less than 1 nm do not exist as a discrete phase (van Olphen, 1977). In practice, it is difficult to know the exact size of a suspended particle because of the difficulties in fractionation techniques and setting the lower limit. Therefore, Nelson and Orlandini (1986) consider all particles with effective diameter less than 1 μm as colloids.

Composition and Sources of Colloids

Chemical composition and reactivity of colloids in natural aquatic systems vary due to different sources (Harnish et al., 1994). Soil clays, and humic substances, in isolation or in association, are soil colloidal components that are most involved in the binding and potential mobilization of anthropogenic chemicals. The components of soil colloids can be conveniently grouped into three categories: layer silicate clays, oxides (including hydrous oxides) and organic matter (Swift and McLaren, 1991). The colloids in groundwater can originate from a number of sources (Keswick and Gerba, 1980; McDowell-Boyer et al., 1986), as by: (1) detachment of colloids such as clay platelets and silicate particles from immobile mineral matrices, (2) in-situ formation due to supersaturated mineral solutes (e.g., iron oxides), (3) growth of viruses and small

bacteria, (4) formation of emulsions or microemulsions of fine droplets (e.g., a colloidal size benzene-water emulsion), (5) agglomeration of macromolecules to form micelles or hemimicelles (e.g., aggregated humic acid molecules) when present at high concentrations, and (6) direct introduction by external sources (e.g., in landfill leachate). In spite of diverse sources, colloids in groundwater are in nature similar to soil colloids. Generally, colloids in porous subsurface environments can be grouped into: inorganic colloids (such as silicate clays and iron or aluminum oxide clays), organic colloids (such as humus), and bio-colloids (such as viruses and bacteria).

Colloid Concentration and Size Distribution

Colloid concentration and size distribution relate to the potential for colloid-enhanced contaminant transport. Data pertaining to colloid concentration and size distribution are commonly reported (Table 2-1). However, determination of these properties can be confounded by artifacts of sampling and analysis.

Because of difficulty in use of direct measurements, a model was initially developed to describe the colloid size distribution for hydrophobic colloids in aquatic systems based on coagulation and sedimentation theory (Lawler et al., 1980; O'Melia and Bowman, 1984; O'Melia et al., 1985; Weilenmann et al., 1989). In the model, the natural water body is segmented into several overlying cells, with the assumption that colloid suspension is spatially homogeneous within each cell. The rate at which the number

Table 2-1. Some examples of colloids observed in groundwater systems.

Ref. [†]	Groundwater System	Techniques [‡]	Size range μm	Concentration
1, 2	Grimsel Site groundwater (Switzerland)	Filtration, SEM, TEM, PC, GRAV.	0.04 ~ 1.0	Number 10^{10} L^{-1}
3	Bad Sackingen groundwater (Germany)	Filtration, SEM	0.01 ~ 0.45	Mass 0.025 mg L^{-1}
4	Cape Cod. MA, Groundwater 1 Groundwater 2	Filtration, PCS	0.078-0.86 0.088-0.82	Mass 2.0 mg L^{-1} 4.5 mg L^{-1}
5	Markham Clinton groundwater (UK)	Filtration, SEM, LIPAS	0.04 ~ 1, Peaks in size distribution: 0.12	Number $10^8 \sim 10^9 \text{ L}^{-1}$
6	Glatt River and groundwater (Switzerland)	Filtration, TOC, metal analysis	0.002 ~ 0.45	Mass 2.3 mg L^{-1}

† 1- Degueldre, 1990; 2- Degueldre et al., 1989; 3- Degueldre and Wernli, 1987; 4- Gschwend and Reynolds, 1987; 5- Longworth, 1990; 6- Waber et al., 1990.

‡ GRAV- gravimetry; LIPAS- laser-induced photoacoustic spectroscopy; PC- particle counting; PCS- photon correlation spectroscopy; SEM - scanning electron microscopy; TEM- transmission electron microscopy; TOC- total organic carbon.

concentration of colloids of size k in cell m changes with time is a function of (i) the rate of formation of colloids of size k from smaller colloids (i, j) that have a total volume v_k in cell m, (ii) the loss of colloids of size k by growth to form larger aggregates in cell m, (iii) the loss of colloids of size k from cell m by settling into the cell below, (iv) the gain of colloids of size k in cell m by settling from above, (v) the input and output of size k colloids by hydraulic inflow and discharge, and (vi) the production or destruction of colloids of size k in cell m. This rate can be expressed as

$$\frac{dn_{k,m}}{dt} = [\frac{1}{2} \sum x(i,j) b(i,j) n_i n_j - n_k \sum x(i,k) b(i,k) n_i]_m + n_{k,m-1} w_{k,m-1}/z_m \quad (1)$$

$$- n_{k,m} w_{k,m}/z_m + n_{k,m}^i q_{m'}^i/z_m - n_{k,m}^o q_{m'}^o/z_m \pm W_{k,m}$$

where n_i , n_j , n_k denote the number concentration of colloids of sizes i , j , k ; x is the coagulation efficiency; $b(i, j)$ is a collision frequency function per unit volume and time, which depends on the physical mode of interparticle approach (such as Brownian motion, fluid shear, and differential settling); $w_{k,m}$ is the settling velocity of colloids of size k in cell m assumed by Stoke's law; z_m is the depth of cell m ; $W_{k,m}$ is the rate of production or destruction of colloids of size k in cell m ; $q_{m'}^i$, $q_{m'}^o$ are the input and output areal hydraulic loadings of cell m ; $n_{k,m}^i$ and $n_{k,m}^o$ are the number concentrations of colloids of size k in the water flowing into and out of cell m .

Particle size distribution can be expressed as a finite number of size intervals which are also chosen as standard particle sizes, based on the logarithm of their volumes (Lawler et al., 1980; Filella and Buffle, 1993). Application of this approach, however, is limited because of many ideal assumptions involved. The expression of particle size distribution varies with the dependent variables. In practice, the results are usually presented as discrete plots of particle volume $\Delta v/\Delta v(\log d_p)$ vs $\log d_p$ (Filella and Buffle, 1993), where the mean particle size is calculated as

$$\bar{d}_p = \sum n_i d_{p,i} / \sum n_i \quad (2)$$

and n_i and $d_{p,i}$ are the number and the diameter of the colloids in size class I, respectively.

The size distribution function $n(d_p)$ of a population of coagulating colloids is defined by

$$\Delta N = n(d_p) \Delta d_p \quad (3)$$

where ΔN is the number of colloids with a diameter in the size interval Δd_p per unit volume of fluid. Bader (1970) observed the size distribution of suspended colloids in sea water, with sizes larger than $1 \mu\text{m}$ to follow a hyperbolic distribution

$$n(d_p) = \Delta N / \Delta d_p = A d_p^{-\beta} \quad (4)$$

where A and β are constants. β typically falls within the range 2-5 and is near 4 in many cases (Lerman, 1979; Osman-Sigg and Stumm, 1982; Simpson, 1982; McCave, 1984). A size distribution with $\beta = 4$ contains equal colloid volumes in logarithmically increasing size grades.

Though this model was established to predict the colloid size distribution over a diameter range $1 - 100 \mu\text{m}$, Filella and Buffle (1993) experimentally verified that it can be applied to estimate the size distribution of colloids with a diameter range $0.1 - 1 \mu\text{m}$ if residence time of aquatic colloids and their initial concentration are specified.

Sampling Techniques for Colloid Characterization

Acquisition of representative samples is essential for accurately characterizing colloids suspended in porous subsurface systems, but constitutes a sampling challenge. Colloid mass, size, and composition are sensitive to disturbance, and hence minimally-intrusive sampling methods are sought. However, many arguments and counter-arguments have been presented regarding the basic principles involved in obtaining a

representative water sample from monitoring wells, piezometers, etc. Controversial aspects of well sampling technique include purging, filtration and pumping velocity.

Korte and Kearn (1985), Barcelona et al. (1985), and the USEPA (1986) discussed groundwater sampling via purging, pumping, and filtering. A traditional groundwater sampling protocol specifies that wells be purged a minimum of three well volumes prior to sampling because the chemistry of water initially stored in the well casing is unrepresentative of the aquifer (Barcelona et al., 1985). However, other studies have questioned the efficacy of purging. Gibbs and Imbrigotti (1990) evaluated well purging criteria and concluded, "...none of the previously recommended criteria for purging a well can be applied reliably to collecting a representative sample of purgeable organic compounds." Robin and Gillham (1987) demonstrated that purging is unnecessary for permeable geologic materials and non-reactive tracers because groundwater in the screened portion of the well is representative of the aquifer.

Influence of sampling techniques on accurate assessment of natural groundwater quality is a particular concern with respect to colloidal concentrations. McCarthy and Wobber (1986) stated that increased flow rate resulting from pumping for sampling purposes may mobilize colloids sorbed to the aquifer material or trapped in low flow zones, and bias chemical analysis results. To minimize these impacts, a sampling pumping rate of 100 mL min^{-1} was recommended by Puls and Barcelona (1989a). However, the determination of pumping rate must be based on the screen area of sampling well and the hydraulic conductivity of the porous medium where the screen is positioned.

In order to minimize disturbances in the well and surrounding aquifer and to prevent mixing of stagnant water in the well casing with water in the well screen, Robin and Gillham (1987) recommended the permanent installation of tubing and pumping at a low rate, thereby eliminating well purging and reducing sampling time and cost. A bladder pump was recommended by Puls and Barcelona (1989a) and Ryan and Gschwend (1990) because its relatively low flow rate would not disturb colloids sorbed to the well casing, screen, sand packer, or aquifer material and therefore would sample only the naturally migrating colloids.

From a hydrodynamic viewpoint, Kearl et al. (1992) applied the colloidal borescope, an in-situ device, providing direct visual means to observe colloids in monitoring wells, and thereby to evaluate the effects of purging, sampling, and filtering. Their findings indicated that purging and filtering are unnecessary, and that sampling from dedicated sampling devices set in the screened interval at low rates are needed to obtain representative water samples. This approach was called the micro-purge low-flow sampling technique by Kearl et al. (1992). A similar sampling technique without purging was recommended by Powell et al. (1993). Most recently, the micro-purge low-flow sampling technique has been further tested and validated by Kearl et al. (1994), Puls and Paul (1995), and Shanklin et al. (1995), respectively.

Fractionation and Analysis of Colloids

Many techniques have been used to fractionate and determine the colloid size distribution (Table 2-1). Classical methods, such as sequential gravimetric analysis following filtration or centrifugation and the Coulter counter, have been widely used for this purpose. However, they are not reliable for colloids below 1 μm , because filtration is prone to lead to a concentration polarization effect by which colloids smaller than pore size (that should pass through the filter) may be entrapped into larger aggregates and retained on the membranes. Obviously, colloid size cannot be inferred only from filter pore size.

With increasing realization of submicro-colloid importance, many advanced techniques have been developed to obtain more accurate measurements. The techniques of free low capillary electrophoresis (CE) (Li, 1992) and field flow fractionation (FFF) (Janca, 1988; Buffle and van Leeuwen, 1993) are promising because of their wide flexibility and avoidance of any stationary phase effects. Moreover, they only require a very small amount of sample for operation, which is particularly helpful to minimize disturbance from sampling through improving sampling design and shortening sampling time. Techniques of light scattering and scanning electron microscopy (SEM) are often applied to delineate the size and number of submicro-colloids, while transmission electron microscopy (TEM) has been thought to be a promising technique due to its high resolution and capacity of adequately minimizing artifacts (Buffle et al., 1989; Perret et al., 1991; Perret et al., 1994; Weel and Goldberag, 1991). Most recently, the advantages

and limitations of photon correlation spectroscopy (PCS) were discussed in detail by Filella et al. (1997). PCS is emerging as a potentially useful technique (Filella et al., 1997; Newman et al., 1994; Rees, 1990; Rees and Ranville, 1990) despite its lower sensitivity for colloidal sizes less than 50 nm.

Minimization of sample processing is particularly important when dealing with colloidal systems. Unfortunately, no in-situ technique is as yet available to directly measure size distribution. Also, most current methods do not allow direct characterization of small colloids in the presence of a high proportion of larger colloids in aquatic systems (Filella and Buffle, 1993). In view of the risk of perturbing the sample derived from size fractionation procedures, the use of a combination of different fractionation techniques and analysis methods are highly recommended in the characterization of colloids (Degueldre, 1990; Perret et al., 1994), especially, combined use of PCS and TEM for the determination of colloid number and size distribution (Filella et al., 1997). However, reliability of TEM technique for this purpose is still questionable because individual colloids probably present in liquid may form aggregates during the drying process.

Mechanisms of Colloid Mobilization

Colloids are ubiquitous in groundwater (McCarthy and Degueldre, 1993). They have been detected in groundwater samples withdrawn from aquifers in a wide variety of geological and geochemical settings at concentrations as high as 100 mg L⁻¹ (Backhus et al., 1993; Buddeemeir and Hunt, 1988; Gounaris et al., 1993; Penrose et al., 1990; Ryan

and Gschwend, 1990; Vilks, et al., 1991; Vilks, et al., 1993). Colloid densities (colloid number) have been reported as high as 10^{10} L^{-1} colloids in granitic rock fractures (Degueldre et al., 1989) and over 10^{12} L^{-1} colloids in a sandy aquifer (Gschwend and Reynolds, 1987). Colloids become suspended in groundwater by a variety of mechanisms.

Colloids can be released to groundwater by dissolution of inorganic cementing agents, such as iron oxides or carbonates, that bind such materials to larger mineral grains (Gschwend et al., 1988; McCarthy and Zachara, 1989). Disaggregation may be induced by a decrease of ionic strength of the groundwater or by a shift of ion balance from one to another (e.g., a shift in dominance from Ca^{2+} to Na^+). Dispersion of particles is promoted by raising pH of the aqueous phase, which increases particle-particle repulsive forces. Mechanical energy of moving water induces colloid mobilization by imposing a shear stress on the matrix, which results in the release of particles into suspension (Kaplan et al., 1993). For example, large rain events lead to miscible displacement of ion-laden soil solution with infiltrating low ionic rain water, thereby dispersing layer silicate clays and fostering their transport from soil into groundwater. Similarly, the artificial recharge of groundwater through soil can lead to turbidity and result in colloid migration to groundwater (Gschwend et al., 1988; Nightingale and Bianchi, 1977). Silica colloids are released during the diagenesis of amorphous silica. Organic macromolecules such as humic substances can be solubilized from kerogen, bitumen, or lignitic materials in the aquifer matrix resulting from microbial activity and abiotic hydrolysis to form colloids. Reduction and dissolution of hydrous oxides may result in the release of clays and

macromolecular organic C adsorbed to the positively charged hydrous oxide surfaces (Ryan and Gschwend, 1990). Siliceous colloids are released into groundwater in calcareous environments because infiltration of waters with different composition dissolves carbonate cements (Gschwend et al, 1988). Possible mechanisms involved in these processes can be described in Fig. 2-1.

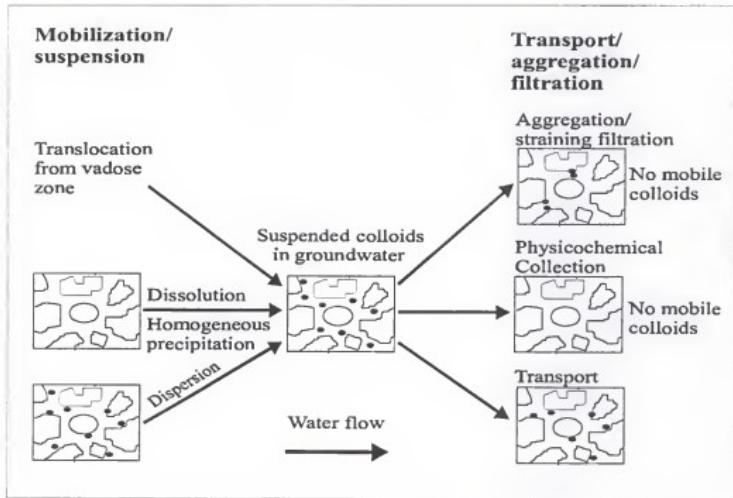


Fig. 2-1. Mechanisms of colloid mobilization in porous subsurface system (dark dots represent individual colloids) (After McCarthy and Zachara, 1989).

Physical Disturbance

Many experiments have confirmed that colloid mobilization due to physical or mechanical disturbance is related to hydrodynamic forces. Hubbe (1987a, b) conducted a comprehensive test of the mechanisms controlling colloid detachment by fluid shear in which spherical colloids ($\text{pH}_{\text{pzc}} = 4.5$) attached to a flat window composed of cellulose film ($\text{pH}_{\text{pzc}} = 3.5$) were exposed to turbulent shear flow, and determined that the rate-determining step in detachment is the initiation of rolling. The critical velocity corresponding to release was found to be in fair agreement with the net adhesive force predicted by DLVO theory, which describes the net effect of the repulsive and attractive forces on the interactions between colloid and grain surfaces (Derjaguin and Landau, 1941; Verwey and Overbeek, 1948), and the characteristic length of the region of contact. Therefore, the balance of torques on a particle adhering to a flat surface in a moving fluid becomes a basis of theories describing colloid mobilization by physical disturbance. The torque balance on the attached particle includes: 1) an adhesive force operating normal to the surface; 2) a drag force operating tangential to the surface; and 3) a lift force operating normal to the surface. The adhesive force binds the particle to the surface while both the drag and lift forces tend to mobilize the particle. Sharma et al. (1992) tested the effects of flow rate, particle size, particle deformability, and solution chemistry (pH and ionic strength) on colloid detachment in flow cell and centrifuge experiments. They found good agreement between the predicted and measured critical hydrodynamic force required for detachment. Characterizing the particles mobilized by water infiltrating

through soil horizons from the Savannah River Plant in Georgia, Kaplan et al. (1993) reported that the abundance of mobilized particles (measured by turbidity) and the size of the mobilized particles (measured by dynamic light scattering) both increased with increasing flow rate during the rainfall simulation, as expected from hydrodynamic detachment theory. The electrophoretic mobility of the mobilized particles was inversely related to flow rate: the particles with the highest zeta potential were mobilized by the lowest flow rates, while high flow rates mobilized the particles with the lowest zeta potential. Particles with lower zeta potential are bound by greater adhesive forces than those particles with higher zeta potential if the surfaces to which they are bound are also negatively charged.

In subsurface porous media, the most common physical disturbance is an increase in the flow velocity by either piezometric head change due to rainfall events or by pumping.

Sampling procedure

Colloid mobilization by groundwater removal and extraction of soil solution is particularly a concern in obtaining representative groundwater samples because colloids are probably mobilized by hydrodynamic shear derived from an accelerated groundwater flow velocity. Observing the impact of sampling rate on particle size through a colloidal borescope inserted in wells (5 cm diameter with 1.5 m length screen), Kearn et al. (1994) found that an elevation of pumping velocity from 100 mL min^{-1} to 1450 mL min^{-1} resulted in a dramatic increase in particle sizes. These results agreed with a similar study on three different sites that showed turbidity increasing sharply in response to pumping

rate increases after a turbidity plateau had been established at a lower pumping rate (Backhus et al. 1993). Therefore, a prolonged slow pumping at a steady rate of about 100 mL min⁻¹ was recommended by Backhus et al. (1993) and Puls and Paul (1995) to avoid artificial mobilization of colloids. A maximum pumping rate of 100 mL min⁻¹ was also suggested by Ryan (1988) for a sandy aquifer with a porosity of 0.4 and hydraulic conductivity of about 4×10^{-4} m s⁻¹. Practically, the proper pumping rate should be determined based on the size of well and permeability of a given porous medium. Recently, the United States Environmental Protection Agency (USEPA, 1995) suggested that the maximum pumping rate for groundwater sampling of colloids and colloid-associated contaminants be the maximum rate at which drawdown does not occur in the formation. Therefore, higher pumping rate may be allowable in more porous or more permeable subsurface media.

Pore water flow velocity

Recharge of groundwater may accelerate water flow near wells. The rapid injection of water can create transient hydrodynamic shear which mobilizes colloids surrounding wells. This effect may be a concern in many small-scale field tests of colloid and biocolloid transport. The rapid addition of the injectates for the test may mobilize naturally immobile colloids or colloids injected and attached in previous tests (Ryan and Elimelech, 1996). Rapid infiltration usually takes place in the vadose zone, though this zone is generally characterized by unsaturated water flow during rainfall events. Heavy rain events could directly cause miscible displacement of ion-laden soil solution with infiltrating low ionic rain water and thereby promote the dispersion and mobilization of

soil colloids. However, it is difficult to verify relationships between rainfall rate and the extent of colloid mobilization based on field observations (Ryan and Elimelech, 1996). Through an experiment on a set of 3*3*1.5 m³ lysimeters containing reconstructed soil profiles of Ap and E horizons, Kaplan et al (1993) found a correlation between the flow rate of water and the resultant colloid concentration. The soil with high pH (6.9) and electrical conductivity (2.3 mS m⁻¹) produced the highest particle concentrations when subject to 10.2 cm of the simulated rain (tap water with pH 6.1 and EC 0.6 mS m⁻¹) over two hours. The abundance of colloids mobilized during higher flow rates were 10.3 times greater than that during lower flow rates. Using a simulation approach, McDowell-Boyer (1992) investigated the mobility of 1.46 μm polystyrene latex (PSL) particles in saturated sand columns at flow rates ranging from 1 to 100 m d⁻¹ and in 1:1 electrolyte solutions from 0.001 to 1 M. Flow velocity has significant influence on mobilization of deposited particles. At the flow rates of 1, 10, and 100 m d⁻¹ using 0.05 M NaCl for each rate, the mobilized PSL particles were respectively 23%, 73%, and 95% of all deposited PSL particles.

Varying pore flow velocity will also lead to changes in colloid properties. For example, increase in flow rate seems to lead to an increase in the mean colloid size in the soil lysimeter effluent though the mass could be decreased with their continuing removal from soil lysimeters. Kaplan et al. (1993) thought that the most obvious mechanism to explain the observation is that as flow rate increased, shear stress imposed on the matrix by moving water increased, thereby liberating larger particles into suspension. Another possible mechanism is that colloid transport efficiency may increase at higher flow rate;



suspensions are prone to move through larger mean pores and have shorter residence times in the profile. Also, larger pores could permit larger particles to pass through the matrix. Conversely, lower effluent flow rate would restrict water flow to smaller saturated pores which probably results in longer residence times of colloids and increases mobile colloid-matrix interaction. The compositions of colloids also tend to vary with the flow rates. The results from lysimeter study (Kaplan et al., 1993) showed that colloids generated during lower flow rates contained 65% more iron oxides and gibbsite, and had 40% greater electrophoretic mobility than colloids generated during higher flow rates, whereas quartz, kaolinite, and HIV (hydroxy-interlayered vermiculite) were enriched by at least 32% in the colloids generated during faster pore water velocities. Total organic C in colloids increased with pore water velocity.

Preferential flows through the whole subsurface during rainfall events may take place due to the existence of worm holes, decayed roots, and other channels in the vadose zone, and the relatively high velocities of infiltration along these channels may mobilize colloids which would be immobile under normal water flow. Similarly, the mobilization of colloids has been reported in fractured aquifers where preferential flow occurs. These colloids are derived from the weathering of primary minerals along the fractures and are immobile in non-fractured media (Degueldre et al., 1989).

Chemical Disturbance

The mobilization of colloids by a change in solution chemistry depends on the alteration of the interface forces between the surfaces of colloids and stationary matrix grains to which they are attached. These forces include a double layer effect, London-van der Waals attraction and short-range repulsive potential energies. However, colloid mobilization caused by change in solution chemistry is mainly attributed to the alteration of double layer potential energy (Ryan and Elimelech, 1996). The double layer potential energy arises from the overlap of diffuse clouds of ions (double layers) that accumulate near charged surfaces to balance the surface charge. If the interacting surfaces are like-charged, the double layer potential energy will be repulsive. If the surfaces are oppositely charged, the double layer potential energy will be attractive. All formulations of the double layer potential energy are sensitive to variations at least in the surface potentials of the colloid and collector and the ionic strength of the solution .

According to DLVO theory (Derjaguin and Landau, 1941; Verwey and Overbeek, 1948), for colloids to be mobilized, the change in solution chemistry must produce repulsive forces between attached colloids and grains that exceed the attractive forces. The interaction potential energy of two charged colloids can be determined by summing the contribution of electrostatic repulsion and van der Waals attraction as shown in Fig. 2-2.

Some model system studies indicate that changes in solution chemistry that produce more repulsive interactions between attached colloids and collectors will

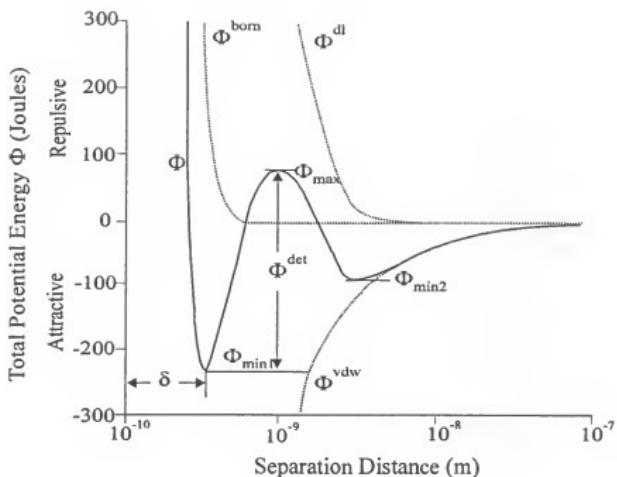


Fig. 2-2. Total intersurface potential energy as a function of separation distance between colloid and grain surfaces. The total potential energy, Φ (solid line), is a sum of the double layer potential energy, Φ^{dl} , the van der Waals potential energy, Φ^{vdw} , and the Born potential energy, Φ^{born} (short-range repulsion energy). A finite primary minimum (Φ_{min1}) is designated by the distance (δ) of the closest approach. The detachment energy $\Phi^{\text{det}} (= \Phi_{\text{max}} - \Phi_{\text{min1}})$ is the energy barrier which a colloid must overcome to escape from its attached state. Φ_{min2} is the secondary minimum at a larger separation distance (After Ryan and Elemelech, 1996; Ryan and Gschwend, 1994).

mobilize colloids (McDowell-Boyer, 1992; Ryan and Gschwend, 1994), though the effects of solution chemistry changes on colloid release can currently be predicted only qualitatively. McCarthy and Degueldre (1993) also pointed out that most of the colloids found in groundwater appear to have been mobilized by changes in the groundwater

chemistry. Theoretically, the following mechanisms can be used to explain colloid mobilization caused by chemical perturbations (Ryan and Elimelech, 1996): 1) colloidal interaction (DLVO theory); 2) energy barrier approach to colloid detachment; and 3) diffusion-controlled colloid release. These changes include increasing pH, decreasing ionic strength, redox potential decrease by infiltrating dissolved organic C, and adsorption of ions and macromolecules that alter mineral surface charge.

Increasing pH

Many model system experiments have shown that increases in pH lead to increases in the release rates and increases in the total amount of colloids. Because an increase in solution pH results in an increment of diffuse double layer thickness between colloids and static grain surfaces. Kallay et al. (1986) tested the release rate of hematite particles which were adsorbed onto spherical glass beads of 110 nm in diameter at low pH (pH 3.2 HNO₃ solution) by suspending the sample in NaOH solutions with pH values ranging from 8.5 to 11.5. Their results showed that the release rate of hematite colloids increased not only with increasing pH of solution, but also in the presence of NaNO₃ (0.01 M L⁻¹). It was confirmed that increase in pH produces repulsive forces that drive colloid release, and that the increase in the extent of colloid release is attributable to a decrease in the retention of colloids on the collectors.

Similar conclusions have been drawn from more recent studies of the effect of pH on colloid mobilization from natural sediments in laboratory columns. Roy and Dzombak (1996) observed that colloid mass released from a 10 cm long Lincoln Sand column with 0.002 M Na⁺ influent (a pore flow velocity of 14.7 m h⁻¹) increased from 150 ppm at a pH

4.0 to 700 ppm at a pH 9.2. Kia et al. (1987) identified a critical pH of 4.8 below which colloid mobilization did not occur in Berea sandstone, a reference porous medium used in the oil and gas industry that contains about 80% dispersible colloids and calcite cement. Ryan and Gschwend (1994) observed a dramatic increase in the rate of colloid release when the pH of a solution passing through an iron oxide-coated sand exceeded the pH_{pzc} value of typical iron oxides, about 7-8. At $pH > pH_{pzc}$, the surface charge of dominant goethite cement binding the kaolinite colloids to the quartz grains was reversed, resulting in repulsive conditions and rapid colloid release. The increase in release rate was qualitatively related to the increase in detachment energy barrier height.

Reducing ionic strength

According to the colloid release theory, a decrease in ionic strength will allow expansion of the diffuse double layers between colloids and static soil matrix surfaces, increase the repulsive interactions, and promote colloid detachment (Kallay et al., 1986; Liu et al., 1995). In an experimental system, Kallay et al.(1986) observed that more hematite colloids were released from glass beads at 10^{-2} M sodium nitrate than 10^{-3} M. Liu et al. (1995) found, in studies on the effect of ionic strength on blocking and colloid transport in porous media, that the extent of colloid release increases with decreasing ionic strength. The rate of blocking increases with decreasing electrolyte strength because of expanded double layers. Increases in pH promote colloid dispersion, and consequently, colloids break through the column at an earlier time. As the ionic strength decreases, colloids attached to small and favorable regions of soil matrix surfaces under

high ionic strength conditions begin to dislodge each other because of the lateral repulsion caused by expanding double layers.

The mobilization of colloids is influenced not only by ionic strength but also by counterion valence. Experiments on the role of solution chemistry in colloid deposition conducted by Liu et al. (1995) revealed that breakthrough curves of both 0.48 μm and 2.51 μm latex colloids suspended in Na_2SO_4 solution (1:2 electrolyte) are totally different from those in the KCl solution (1:1 electrolyte). In the presence of a divalent counterion, SO_4^{2-} , higher initial blocking rates were observed, but little change with time for lower ionic strength and rapid decrease with time for higher ionic strength. The ionic strength of a solution controls the range of particle-particle interaction through its regulation of the double layers thickness, and the presence of specifically interacting counterions can control particle-particle interaction through adsorption and charge neutralization (Elimelech, et al., 1995).

Colloid release in natural porous media (soil and aquifers) is influenced by ionic strength in much the same way as for experimental systems. A decrease in ionic strength is usually caused by infiltration of dilute precipitation water, irrigation by fresh water, or injection of fresh water for artificial recharge or secondary oil extraction. Many experiments reported in the soil science literature (Abu-Sharar et al., 1987) have demonstrated that dilute solutions composed of monovalent ions are most effective in mobilizing colloids and reducing hydraulic conductivity in saturated soils and in flow through soil columns, while little or no mobilization of colloids occurs in solutions of higher ionic strength and solutions containing divalent ions. Roy and Dzombak (1996)

revealed that the total mass of released colloids from Linchon Sand columns increased sharply (from 60 ppm to 12500 ppm) with a greater reduction in ionic strength of NaHCO₃ from 0.05 M to 0.001M at pH 9.2. Although effluent colloid concentrations were extremely high in some of their experiments with low ionic strength, there was no significant decrease in permeability. As a result of colloid release, the specific surface area of the sand diminished substantially. For release at 0.001 M, the specific surface area changed from 3.2 m²g⁻¹ in the original sand to 0.9 m²g⁻¹.

In heterogeneous porous media (such as most soils and aquifers), colloid mobilization caused by a decrease in ionic strength tends to reduce hydraulic conductivity because of colloid deposition in narrow pore throats. Aquifers and geologic formations which are susceptible to such reductions are termed *water sensitive* (Khilar and Fogler, 1983). Brown and Silvey (1977) observed decreases in hydraulic conductivity when fresh water was injected into a brackish aquifer to replace sea water in the coastal plains of Virginia. This effect depends on the mineralogy of a given medium. The presence of expanding clay minerals such as montmorillonite can produce much greater reductions in hydraulic productivity than the presence of illite or kaolinite (Goldenberg et al., 1982).

Adsorption of surfactants

Adsorption of surfactants to colloid and grain surfaces can lead to colloid mobilization due to the surface charge alteration (e.g. reversing the surface charge of mineral surfaces) (Liang and Morgan, 1990).

Infiltration of organic matter-rich water from a swampy, intermittent stream caused colloid mobilization in a quartz sand coated mainly by goethite and kaolinite in

the New Jersey Pine Barrens, because the infiltrating organic matter produced reducing conditions which caused the dissolution of the goethite (Ryan and Gschwend, 1990). Because of the lower clay concentration where the goethite content was lowered by dissolution, it was surmised that colloids found in the groundwater had been mobilized by decementation of the coatings, i.e. the removal of the positively-charged goethite led to repulsive interactions between the negatively-charged kaolinite colloids and quartz grains. However, goethite dissolution is not always necessary for colloid mobilization. Ryan and Gschwend (1994) tested the effect of dodecanoic acid and natural organic matter on the mobilization of colloids from goethite-coated sands. Concentration of dodecanoic acid (RCOO^-) of about $16\text{-}48 \mu\text{M}$ began to cause a dramatic increase in the colloid release rate because the formation of hemimicelles (at about $24\text{-}240 \mu\text{M}$ dodecanoate) on the goethite surfaces resulted in a reversal of surface charge without dissolving goethite. In the presence of dodecanoic acid, the release rate of clay was largely enhanced by an increasing pH. For the same porous medium, experiments revealed that natural organic matter (NOM) mobilized clay more rapidly than it dissolved Fe, which suggested that the NOM caused clay mobilization in the same manner as the dodecanoic acid (for a given clay release rate, both solutions contained almost the same concentrations of carboxyl functional groups). These data also suggest that NOM mobilizes kaolinite colloids by adsorbing to the goethite and reversing the surface charge (Ryan and Gschwend, 1994).

Implications of Colloid Transport

Colloid Transport through Porous Media

Field observations and experiments have demonstrated that some types of traceable colloids, such as polystyrene microspheres, bacteria, and viruses, are transported through aquifers at rates comparable to conservative solute tracers (McKay et al., 1993; Rossi et al., 1994). These traceable colloids in both porous and fractured media typically suffer substantial attenuation over the short distances of these field tests (about 1-10 m). As groundwater tracers, bacteria and viruses transport over the distance up to 1.6 km has been observed in fractured aquifers (Keswick et al., 1982).

Investigations of colloid transport in natural aquifers are limited by the ability to detect the injected colloids in downstream monitoring wells. Owing to this difficulty, much of our knowledge of colloid transport in groundwater comes from experiments testing the mobility of bio-colloids, viruses, and bacteria, in aquifers. The factors controlling the transport of bio-colloids in porous media have been reviewed by Harvey (1991 and 1993). Many of these studies have included co-injections of polystyrene latex microspheres, which can be detected in samples by epifluorescence microscopy. In the study tracing the transport of inorganic colloids injected into an aquifer, Higgo et al. (1993) injected 25 nm silica colloids into a sandy, iron oxide-coated aquifer at Drigg, Cumbria, UK. the silica colloids were detected by light scattering. Over nearly 2 m of

transport , only 12% of the silica colloids were lost by deposition to the aquifer material.

Silica breakthrough was approximately coincident with a tritiated water tracer.

Furthermore, many models have been developed to delineate colloid transport in subsurface. For instance, phenomenological approach, trajectory approach, and network approach have usually been used to model the transport of colloids in porous media. Phenomenological models are built based on the mass balance of a slice of a porous bed for predicting particle concentration history at any location within the bed and do not involve the pore structure which is an important factor for particle capture within the bed (Amirtharajah, 1988). Trajectory models focus on microscopic analysis of individual particle trajectories. For example, a numerical model, VIROTRANS (Tim and Mostaghimi, 1991), was developed for simulating the vertical transport of water and virus through soils treated with waste-water effluents and sewage sludge. Another example of Trajectory models is the Deep bed filtration (DBF) model that simulates a process in which colloids present in the flowing suspension deposit at different locations along flow paths within porous media. Network model approach has been applied to simulate colloid movement through a network of individual channels and junctions (Rege and Fogler, 1988; Imdakm and Sahimi, 1987). Several types of networks such as square, voronoi, single hexagonal, and triangular have been used to represent the porous media, of which the voronoi network seems to be preferred due to its random nature and more efficient flow calculation.

Pedogenic Processes

The movement of colloidal-sized particles in soils as well as aquifers have been confirmed by many investigations. A greater mobility and dispersibility of fine clays relative to coarse clays were indicated by clay translocation with a higher ratio of fine clay to total clay in the illuvial soil horizon compared to the eluvial horizon (Gschwend et al., 1988). However, the mobility of colloids is greatly influenced by pore size distribution of porous media (soils), particle size distribution of colloids themselves, etc. Thus, sandy textured soils with larger pore size and narrow pore size distributions should be more conducive to colloid transport due to a dominant role of size exclusion in inhibiting the colloid migration through the porous media (Ouyang et al., 1996). In most cases, the transport of illuviated clays has been thought to be limited by deposition near the water table, where the velocity of the filtrating water decreases.

In the formation of soils, colloid mobilization and transport are two of many inferred processes based on laboratory analyses and field observations (McDowell-Boyer et al., 1986). Movement of suspended colloids (clay) within soils, as a well-documented process, ultimately results in horizons of clay depletion (eluvial) overlying horizons enriched in clay (illuvial or argillic) (Birkeland, 1984; Boul et al., 1980; Fanning and Fanning, 1989; Jenny and Smith, 1935; McKeague and St. Arnaud, 1969; Soil Staff, 1975.). Soil horizon patterns such as A - E - Bt ..., A - E - Bh ..., etc., are self-evident expressions of these processes.

The USDA Soil Taxonomy (Soil Survey Staff, 1975, 1996) places a heavy emphasis on eluviation or illuviation in defining diagnostic horizons. Colloid migration within soils has been evaluated using a variety of radio-labelled colloidal suspensions such as those labeled by ^{86}Rb (Bertrand and Sor, 1962), ^{32}P (Kazuo and Gruber, 1962), ^{90}Sr (von Reichenbach and von der Bussche, 1963), ^{60}Co (Toth and Alderfer, 1960), ^{59}Fe (Coutts et al., 1968a and 1968b), etc. Birkeland (1984) noted the difficulty in isolating specific processes that control the translocation of colloidal materials such as iron, aluminum, layer silicates, and organic matter. However, the concepts of colloid mobilization help explain observed features of soils. Aqueous pH and ionic composition control clay and organic matter aggregation and attachment. Pilgrim and Huff (1983) found that rainfall causes colloids to be released from soil aggregates into suspension, and recorded suspended sediment concentrations of over 1000 mg L⁻¹ in subsurface flows. These suspended colloids along with other soluble materials either accumulate at some depth in the soil or pass through to the groundwater system, depending on filtration and other factors influencing flocculation and precipitation.

Colloid-Facilitated Transport

Soils and aquifers are complex porous media in which mobile colloids can potentially enhance contaminant migration. Advective-dispersive models of contaminant transport which assume an immobile sorbent would underestimate contaminant migration distance in cases where colloids are moving within the system. In effect, the colloids

would in these cases constitute a mobile sorbent. The mobility of such a sorbent is dependent upon the mobility of the colloids as well as the retention-release processes. Therefore, soils and aquifers with a mobile colloid component can be characterized as three-phase systems: an aqueous phase, a carrier phase, and a stationary solid matrix phase. An air phase should also need to be considered in the case of unsaturated soils (Choi, 1995) involving volatile chemicals.

When contaminants have appeared at distances in porous subsurface systems greater than those anticipated based on two-phase partitioning between solution and stationary phases, colloid-facilitated transport has been invoked as a possible explanation (Ryan and Elimelech, 1996). Penrose et al. (1990) detected colloid-associated Pu from a radioactive waste source in an alluvial deposit at Los Alamos National Laboratory. Based on two-phase partitioning theory, a tritium transport velocity of $v_{\text{tritium}} = 3.4 \text{ km yr}^{-1}$, a bulk density to porosity ratio of $\rho_b/n = 8$, and a K_d value of 10^4 mL g^{-1} (measured for Pu interaction with the colloidal material), Pu is predicted to migrate at a velocity of only 4.2 cm yr^{-1} using the retardation formula (Freeze and Cherry, 1991). As shown in the Fig. 2-3, the actual Pu transport velocity was measured at nearly 500 m yr^{-1} , which is 1200 times greater than the predicted transport velocity. The enhanced Pu transport velocity may be attributed to local nonequilibrium or preferential flow paths, but the evidence collected by Penrose et al. (1990) suggested that the Pu was transported with colloid phases. A simple modification of the K_d approach to account for the presence of colloidal phases is designated as three-phase partitioning in Fig. 2-3. Surprisingly, the addition of a mobile colloid phase into the retardation formula does not improve the prediction of Pu transport.

Using 10 mg L⁻¹ colloids and the same K_d value for Pu association with both the stationary and mobile sorbent, the predicted Pu transport velocity is only 4.7 cm yr⁻¹.

The effect of colloids on Pu transport is predicted to be insignificant even though an assumption of conservative transport of colloids was made to the retardation formula. If colloid filtration is considered, the difference between the two-phase and three-phase Pu transport predictions will become even smaller. Gounaris et al. (1993) obtained similar predictions using the three-phase retardation expression to account for the effect of colloids on contaminant transport in a landfill leachate plume. Obviously, colloid transport is not conservative, and simulation models of colloid-facilitated transport are also unable to explain the unexpectedly great migration distances observed in the field studies. Firstly, colloid transport in most aquifers will be limited to distances of meters to tens of meters under typical conditions based on classical colloid filtration theory (Elimelech et al., 1995). Secondly, the Kd value used in the existing models (both 2-phase and 3-phase) for the stationary aquifer sediments is probably different from that for the mobile colloids, and the constant Kd approach is not appropriate for most inorganic solutes because their sorption is nonlinear (McCarthy and Zachara, 1989). Finally, the enhanced transport of contaminants is likely promoted by submicro colloids (< 1000 nm in size), whereas the latter is not accurately predicted by the classical colloid filtration theory. Therefore, a need exists for improving the simple classical model so that it is able to more accurately describe colloid-assisted contaminant transport with a concern of submicro colloids.

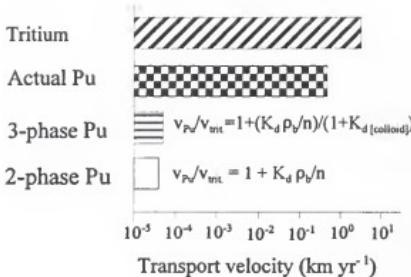


Fig. 2-3. Expression of the data reported by Penrose et al. (1990). *Tritium* velocity refers to conservative transport rate of tritiated water; *Actual Pu* velocity refers to the observed transport rate of plutonium tracer; *2-phase* velocity and *3-phase* velocity refer to the predicted Pu transport rate in absence of colloids and in the present of 10 ppm colloids, respectively. Assuming K_d holds constant for Pu adsorption to both the aquifer matrix and the mobile colloids.

In fact, many models have been developed to deal with the colloid-facilitated transport issue, such as COMET model (conceptual colloid-metal transport) (Mills et al., 1991), three-phase models (Jiang, 1993), the four-phase model (Choi, 1995), the biofilm models (Corapcioglu, 1995; Johson, 1995; Saiers, 1996; Vilks 1996), etc. Unfortunately, the existing models addressed above almost ignored to verify whether or not mobile colloids are present and transport. Therefore, Buddeemeir and Hunt (1988) and Penrose et al. (1990) commented that transport of colloids over hundreds of meters to kilometers may be inferred from facilitated transport observations. That contaminants are associated with colloids at the monitoring locations, however, is not enough to prove colloid transport. Given that the mobilization of colloids in concentrations sufficient to affect

contaminant transport requires the kind of chemical perturbations occurring in contaminant plumes, it is unlikely that these colloid concentrations will be maintained beyond these plumes. Thus, it has been suggested that future researches of colloid-facilitated transport must include verification of colloid transport from waste source to monitoring points to prove that colloid-facilitated transport is responsible for enhanced contaminant migration. Furthermore, Ryan and Elimelech (1996) emphasized that, when examining the discrepancy between predicted and actual contaminant transport distances in porous subsurface systems, the following criteria for colloid-assisted contaminant transport have to be considered: 1) colloids must be present; 2) contaminants must associate with the colloids; and 3) colloids and associated contaminants must be transported through the groundwater.

Summary

Prediction of the potential for colloid-enhanced transport requires an understanding of the mechanisms of colloid mobilization, not only in saturated media such as groundwater in surficial or unconfined aquifers, but also in the unsaturated vadose zone. Mobilization of colloids is strongly influenced by such variables as colloid surface properties, pore size distribution of soils or aquifers, pore water flow velocity, pH and ionic strength of soil solution, etc. Among these, pore water flow velocity is a particularly critical factor influencing colloid mobilization in the vadose zone. Models for colloid transport and colloid-facilitated transport are generally limiting.

Reliable characterization of colloids can be an analytical challenge, but is essential for understanding colloid movement in groundwater, and for evaluating the role of vadose-zone-borne colloids in the fate of contaminants in a given subsurface environment. Submicro-colloids (1 to 1000 nm) are likely the most important colloidal phase with respect to the environment, but are poorly understood. Accuracy in characterizing submicro-colloids has been improved with the development of more powerful models and advances in particle technologies and sampling protocols. Promising analytical approaches include transmission electron microscopy (TEM), field flow fractionation (FFF), photon correlation spectroscopy (PCS), capillary electrophoresis (CE), etc., and their combination.

CHAPTER 3

SOIL- AND HYDROLOGICAL CHARACTERIZATION OF THE STUDY SITE

Introduction

The overall goal of this research was to determine the extent to which concentration and composition of colloids in groundwater are influenced by groundwater dynamics and the nature of the soil matrices. This chapter characterized groundwater dynamics and soil morphology at the study site, and discussed relationships between watertable trends and soil horizon surfaces. Thus, the information provided here serves as background for Chapter 4, which specifically addresses the nature of colloids suspended in groundwater sampled at the site.

Aquods are prevalent soils within flatwoods landscapes of the lower Atlantic and Gulf Coastal Plains in the Southeastern U.S. (Brasfield et al., 1973). Flatwoods are characterized by a nearly-level topography, a shallow, fluctuating watertable (Brown et al., 1990), and pine-forest ecosystems (Abrahamson and Hartnett, 1990). The prevalence of Aquods on flatwoods, in conjunction with the scarcity of Spodosols on better-drained landscapes of the region, suggests that fluctuating watertables are a factor in Aquod genesis. Hypotheses regarding the prospective roles of the watertable in the genesis of E - Bh horizon sequences typical of Aquods have been proposed and tested in the laboratory

(Harris et al., 1995), and field studies contrasting hydrological characteristics of Aquods and associated soils (Garman et al., 1981; Hyde and Ford, 1989) have been conducted.

The Bh horizon of Aquods generally occurs within the zone of the fluctuating watertable, but the depth to its upper boundary does not necessarily relate to mean watertable depth (Hyde and Ford, 1989). Likewise, the depth of experimentally-generated Bh-like features (darkened zones underlying stripped sand) vary markedly despite identical watertable fluctuation conditions (Harris et al., 1995); nevertheless, these features do not develop under freely-drained conditions with the same water flux. Hence, a state of saturation, for some minimal duration, appears to be a factor in initializing podzolization in the region.

Additional evidence that the watertable is a critical factor in Aquod genesis can be found at Aquod boundaries with better-drained soils. This transition zone commonly displays a trend in which the Bh horizon becomes thinner, shallower, and lighter in color until it merges with the A horizon of the adjacent better-drained soil, as has been confirmed by field-experienced soil scientists of the region (personal communications, Dr. V.W. Carlisle and Mr. Frank Watts). Precise correspondence between an upward-fading Bh and a downward-sloping watertable was documented earlier by Garman et al. (1981).

Such transitions at boundaries between Aquods and better drained soils provide an opportunity to distinguish the specific hydrological conditions most critical to the formation of E - Bh horizon sequences in Aquods. They also encompass a range in hydrological and morphological conditions that could influence the nature and

composition of groundwater colloids within the flatwoods soils. This study was conducted along a relatively abrupt (<5 m) Aquod-Udult soil boundary (Fig. 3-1) similar to the one studied by Garman et al. (1981). Objectives were to (1) compare the Aquod and Udult soils with respect to depths and duration of saturation, (2) determine hydraulic responses of horizons to rainfall events along the Aquod-Udult transition, and (3) provide background information for the characterization of groundwater colloids in Chapter 4.

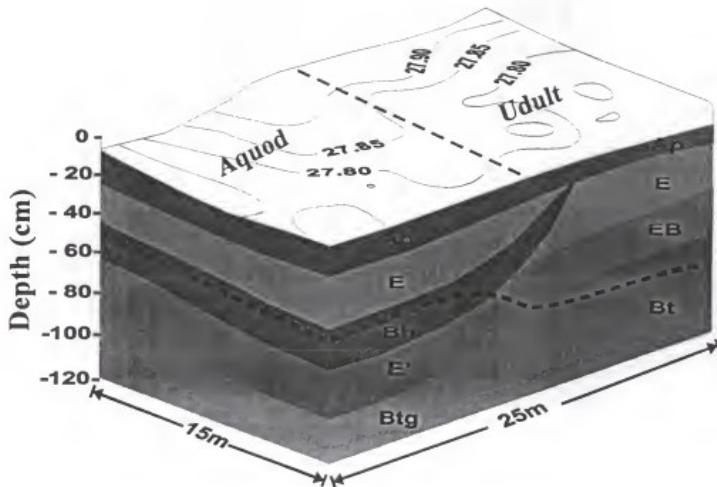


Fig. 3-1. Schematic cross-sectional configuration of soil horizons as related to the prevailing groundwater surface trend (thick dashed line) across the Aquod-Udult transition at the study site.

Materials and Methods

Study Site

The study site is on a landscape of flatwoods and depressions located 33 km northeast of Gainesville, Florida (Fig. 3-2). Current vegetation is mainly young longleaf pine (*Pinus palustris* Miller, 7 years old now) and slash pine (*Pinus elliottii* var. *elliottii* Engelm.). The dominant soils in the vicinity of the site are Pomona series (sandy, siliceous, hyperthermic, Ultic Alaquods) (Crownover et al., 1995), with inclusions of Lochloosa series (loamy, siliceous, hyperthermic, Arenic Paleudults). The average annual temperature is 21°C, with a mean monthly temperature ranging from 14 °C in January to 27 °C in July. Average annual rainfall is about 1330 mm with two distinct dry periods (April - June; October - December).

The specific area of study represents a catena consisting of an Ultic Alaquod, Arenic Paleudult, and a narrow transitional zone between these soils. The boundary was delineated by hand augering. A representative pedon within each soil was described and sampled, and particle-size distribution was determined by a pipette method (Gee and Bauder, 1986) (Table 3-1).

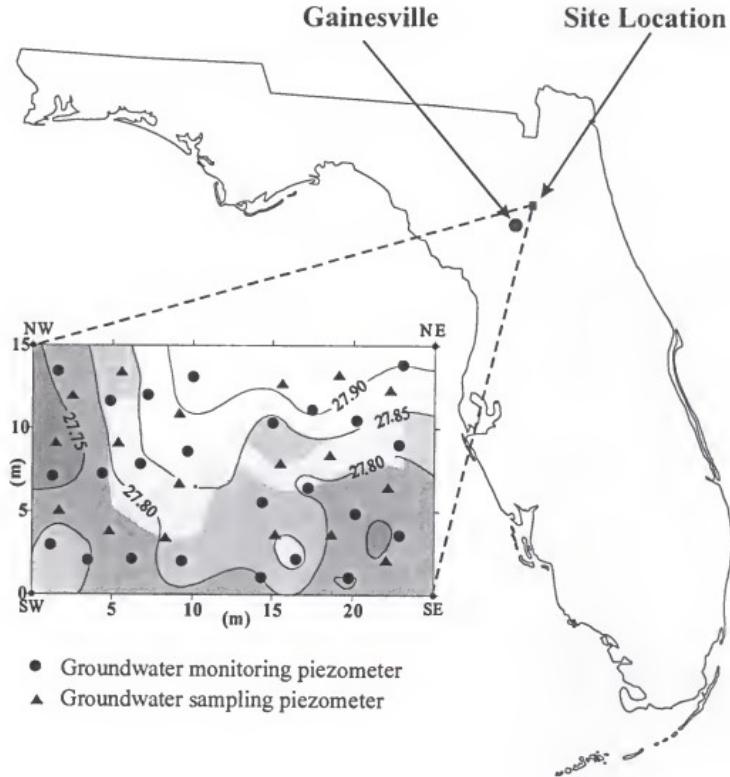


Fig. 3-2. Site location, topography of ground surface and piezometer distribution at the study site.

Table 3-1. Selected properties of soils at the study site.

Soil	Horizon	Depth cm	Munsell Color	OC (%)	Sand (%) 2-0.05mm	Silt (%) 50-2 μ m	Clay (%) $\text{d}_{2\mu\text{m}}$	Texture (USDA)	FST/S [†] (cm h ⁻¹)	K _{sat} [‡] (cm h ⁻¹)
Aquod	Ap	0-18	10YR 3/1	2.4	93.5	4.0	2.6	sand	0.48	
	E	18-30	10YR 5/2	0.4	96.3	2.9	0.9	sand	0.50	
	Bh1	30-38	10YR 2/2	2.9	90.8	3.5	5.7	sand	0.59	
	Bh2	38-55	10YR 3/3	2.2	91.9	7.8	0.3	sand	0.60	40.0 ± 8.0
Ultid	E'1	55-68	10YR 5/3	0.6	94.5	4.2	1.3	sand	0.62	
	E'2	68-85	10YR 6/2	0.2	96.0	2.7	1.3	sand	0.56	76.0 ± 9.0
	Btg	85-97+	10YR 6/2	0.2	82.5	2.7	14.8	sandy loam	0.56	3.3 ± 0.9
Ultid	Ap	0-10	10YR 4/1	1.7	94.2	3.5	2.3	sand	0.55	
	E	10-50	10YR 5/4	0.2	92.9	4.7	2.4	sand	0.62	27.0 ± 1.5
	EB	50-65	10YR 5/8	0.3	86.9	5.1	7.9	loamy sand	0.59	18.3 ± 1.8
	Bt	65-95+	10YR 6/4	0.3	66.8	2.4	30.8	sandy clay loam	0.64	0.8 ± 0.4

[†] Ratio of fine sand and total sand. [‡] Saturated hydraulic conductivity (geometric mean, n = 4).

Installation of Monitoring Piezometers

Each monitoring piezometer was constructed of a 152-cm long hollow PVC pipe having a 3.5-cm inside diameter and 4.0-cm outside diameter. The end of the pipe serving as the piezometer inlet (below ground surface) was blocked, and a screen extending 5 cm upward from the blocked end was created by drilling small holes into the pipe. A removable cap was used to cover the outlet (above ground surface) in order to prevent rain entry but allow air flow after the piezometer was installed.

Monitoring piezometers were installed (in quadruplicate) in Bh, E', and Btg horizons within the Aquod area and in E, EB, and Bt horizons within the Udult area. They were deployed according to a block design, in which each horizon was considered a treatment. Thus, there were 3 treatments x 4 replicates x 2 soils, totaling 24 piezometers. Piezometers were randomly assigned in a grid pattern (2.5 x 2.0 m²), but avoidance of stumps, large exposed roots, and harvesting rills prevented regular spacing within the grid blocks (Fig. 3-2).

Piezometers with a 4.0-cm outside diameter were installed as follows: A 10-cm diameter hole was augered with a bucked auger to the top of the horizon where a piezometer screen was to be positioned. Then a 4.0-cm diameter hole, 12 cm deep, was drilled in the bottom center of the 10-cm diameter upper hole. The piezometer was carefully driven into this smaller hole to the appropriate depth. Then, wet concrete was used to seal the upper pipe within the upper hole. The depths of piezometer placement were dictated by horizon depth for the relatively thin Bh and E' horizons of the Aquod

and for the EB horizon of the Udult. However, all Btg and Bt horizon piezometers were installed at the same elevation, as were E horizon piezometers of the Udult. The Btg, Bt, and E horizons were thick enough that constant elevation placement was possible, thus providing upper and lower elevational planes of reference.

Watertable Monitoring and Representation

The watertable has been defined as "the upper surface of groundwater or that level in the ground where the water is at atmospheric pressure" (Soil Science Society of America, 1997). Below the watertable the water pressure (P) is positive (i.e. greater than atmospheric pressure), and the soil is generally assumed to be at or near saturation; whereas above the watertable, P is negative and soil is unsaturated above a capillary fringe region. Piezometers provide a means for monitoring total piezometric (hydraulic) head $[H(z) = h(z) - Z]$ in saturated groundwater where h is positive water pressure head at a given soil depth z and Z is the depth below the soil surface (note: $H(x,y,z) = h(x,y,z) - Z$ where $Z = 0$ is an arbitrary gravitational datum set at the soil surface, and $h = 0$ is a reference here). Spatial differences in $H(x,y,z)$ at any given time can be used to calculate the driving force as well as the direction of groundwater flow. In general, flow tends to occur from high H region to low H region. Strictly, under hydrostatic groundwater conditions (no flow), piezometers can also be used to monitor the watertable depth Z_{wt} (where $h = 0$) (Koorevaar et al., 1983). Therefore, piezometers were selected for this study. The total piezometric heads for sandy upper horizons of the soils corresponded

very closely to the level at which water would flow into an auger hole, and hence were approximate indicators of the watertable as defined above. However, the heads of the underlying argillic horizon did not always correspond to those of the coarser-textured horizons (as discussed below), which indicates the influence of dynamic water flow through the layered soil profile. Piezometric head losses spatially through a soil profile is always an indicator of flow conditions. Differences in saturated hydraulic conductivity can greatly accentuate head losses in layered soils. Therefore, for the purpose of this study, a distinction was made between the piezometric surface of the argillic and that formed within the overlying horizons.

Piezometric heads were normally determined once a week from August 1996 through August 1997 using a scaled float-rod. In addition, special short-term monitoring was performed to determine the nature of watertable variations following some rainfall events. Topographies of piezometric- and soil horizon surfaces were interpolated via Kriging (Dunlap and Spinazola, 1984).

Field Estimation of Hydraulic Conductivity

The vertical recharge rate of water (flux Q) into a piezometer depends on the total hydraulic head gradient ($\partial H / \partial Z$; ratio of hydraulic head difference over elevation difference). According to Darcy's equation, the hydraulic conductivity (K) is the proportionality constant relating flux to hydraulic head gradient (the effect of horizontal flow is neglected here):

$$q_z = -K_z \partial H / \partial Z$$

or $Q_z = -AK_z \partial H / \partial Z \quad (1)$

where Q_z is the vertical recharge flux or volume of water passing into the piezometer per unit area of screen per unit of time, q_z is the Darcy water flow velocity (distance per time), K_{sat} is the saturated hydraulic conductivity, and the A is the piezometer screen area. For small time increments, the ordinary differential relation (1) can be presented in the simple numerical difference form as follows:

$$q_z = -K_z (\Delta h / \Delta z - 1)$$

or $Q_z = -AK_z (\Delta h / \Delta z - 1) \quad (2)$

where z represents the depth below the soil surface.

Determination of Q_z was conducted after a heavy rainfall within an exceptionally wet period (January, 1998) when all soil horizons were saturated and hydraulic heads were near maximum. The procedure was as follows. The initial hydraulic head (h_1) was recorded as the reference level at the soil surface (h_1 and $z_1 = 0$). Flexible sampling tubing was inserted into piezometers such that the inlet of the tubing was positioned 5 cm above the piezometer bottom (i.e., at the top of the screened zone). Water above the tube inlet level (which established h_2 and $z_2 = 0$) was pumped out of piezometers. The pumping rate was then adjusted to maintain the water level within the piezometer at the top of the screened zone, and the volume of water subsequently pumped per unit time was determined. Total volume withdrawn was about 400 mL for sandy horizons and 50 mL for argillic horizons. Water entry was so slow for the latter that a 2-h interval was required for sufficient water quantities to be withdrawn. The change in gradient for the

interval was trivial relative to the total gradient (assuming no drawdown when pumping), however. This procedure set up an approximate steady-state flow in saturated soil, such that the hydraulic gradient could be calculated as $\partial H/\partial Z = -1$ ($\partial H/\partial Z = \partial h/\partial z - 1$ while $\partial h/\partial z = 0$), and equation (2) becomes

$$Q_z = AK_{\text{sat}}$$

and $K_{\text{sat}} = Q_z/A$ (3)

Screen area A is known, and is equal for all piezometers. Saturated hydraulic conductivity K_{sat} was calculated using equation (3) and listed in Table 3-1.

Results and Discussion

Piezometric heads were consistently higher in the Aquod than in the Uduto (Fig. 3-3), though differences for upper sandy horizons were minimized for brief periods following heavy rains (Fig. 3-4). In effect, the highest seasonal piezometric readings for the Uduto closely approached those of the Aquod, but duration of saturation in the sandy zone was much less for the Uduto (Fig. 3-5). Piezometric surfaces of all horizons tended to be steepest at the boundary between the soils (Fig. 3-4), verifying close correspondence between soil and hydrological transitions. The zone of steepening corresponds closely to the abrupt morphological transition; specifically, slopes of the Bh horizon and piezometric surfaces were opposite in direction, but in mutual correspondence to the boundary (Fig. 3-1). The morphological-hydrological trends along the boundary were similar to those reported by Garman et al. (1981).

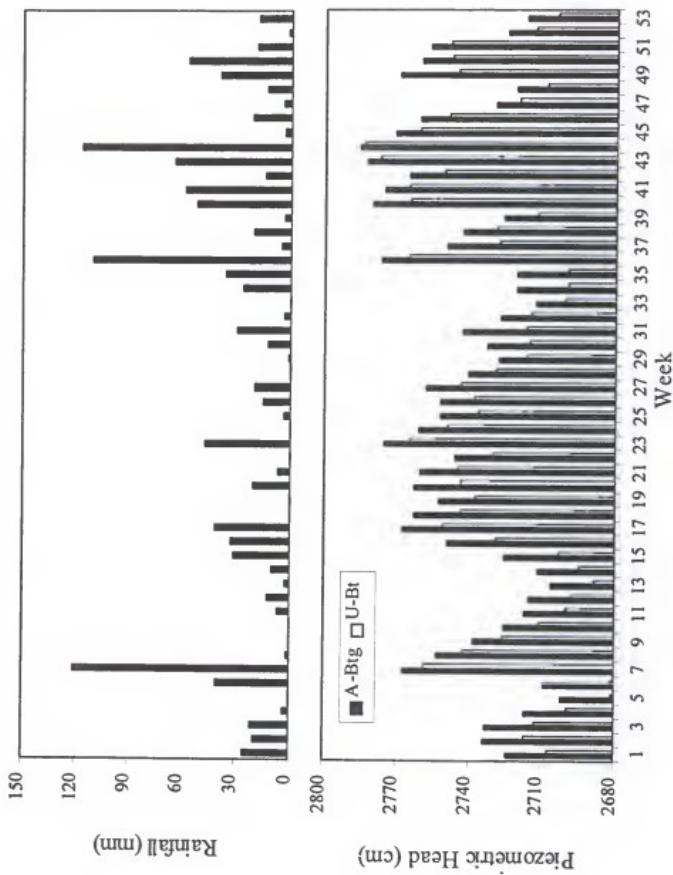


Fig. 3-3. Comparison of weekly fluctuations of rainfall and piezometric head of Aquod Big- and Uduto Bt horizons from August 29, 1996 through August 29, 1997 (Rainfall data were collected from an automatic recording station about 300 m far from the research site).

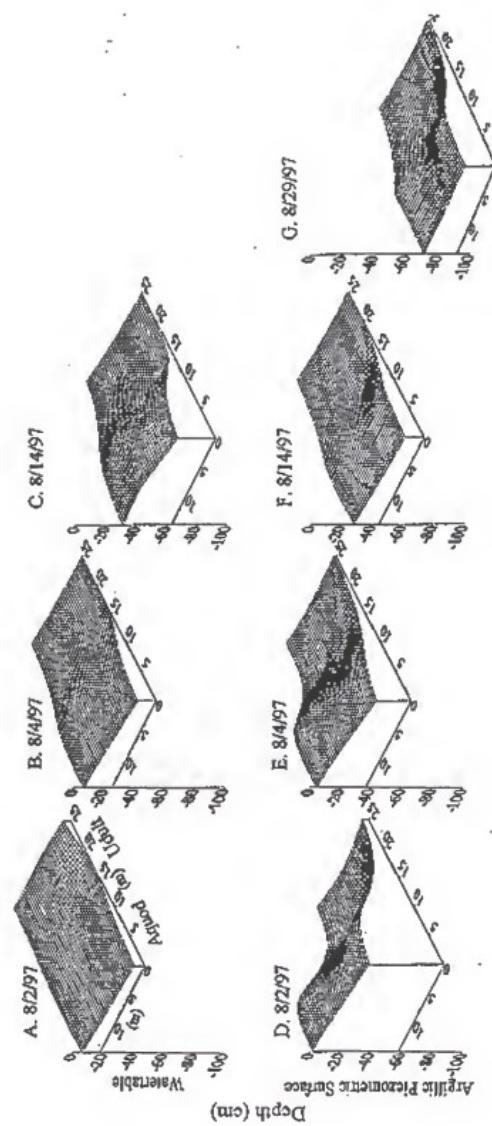


Fig. 3-4. Piezometric surfaces at specified dates during a wet-to-dry period. The depth value of zero represents the highest ground surface elevation on the experimental site. Letters A through C represent the piezometric surface formed in upper sandy horizons (Bh, E', E, and EB), which constitutes the waterable; and D through G represent the piezometric surfaces formed in argillitic horizons (Btg and Bt). On 8/29/97, water was present only in the E horizon of the Aquod, and in the argillitic horizons of both soils. A "lag" in the Uduilt argillitic response to the rainfall event is evident from comparing A and D. During the dry period the Uduilt argillitic eventually "catches up", while there is a concomitant general lowering of all piezometric surfaces.

The argillic-horizon hydraulic head was commonly below the upper boundary of the horizon within the Uadult area, but was continually above the upper boundary of the horizon in the Aquod area. The Aquod argillic was, in effect, under long-term artesian conditions with respect to its own surface, supporting a watertable in the overlying sandy horizons for long periods. The better-drained conditions of the upper part of the Uadult argillic horizon is in accord with the near absence of redoximorphic features in the upper 10 cm; redox depletions and concentrations are evident in the upper part of the Aquod argillic. The absence of the E - Bh sequence in the Uadult coincides with unsaturated conditions for >50% of the time in the upper sandy zone (Fig. 3-5).

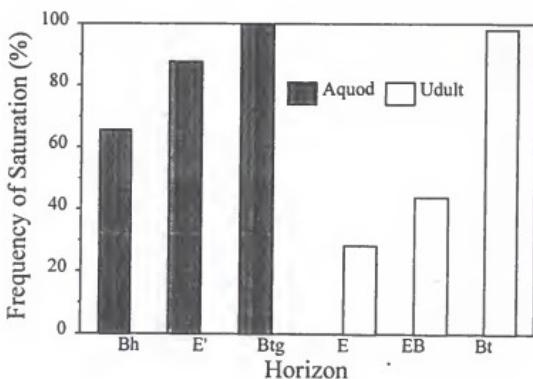


Fig. 3-5. Frequency of saturation, by soil and horizon, based on the percentage of observations for which measurable water was found in piezometers installed in the horizons during the annual monitoring period.

Freeze and Cherry (1979) stated that in a confined aquifer, water level in a well typically rises above the top of the aquifer due to artesian conditions, whereas in an unconfined aquifer, the groundwater table forms the upper boundary. So, the Aquod Btg- and Uadult Bt horizons behave hydraulically like "semi"-confined aquifers where K_{sat} values of these layers are very small relative to the upper sandy zones which constitute an unconfined aquifer (Fig. 3-6).

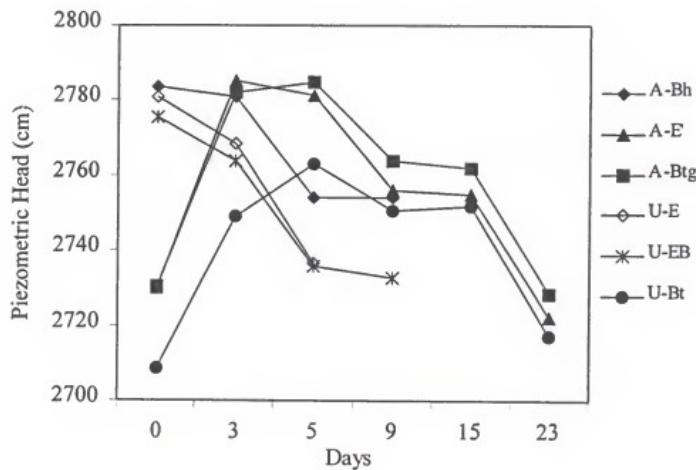


Fig. 3-6. Piezometric head variation of horizons in response to a rainfall event (about 50 mm) which occurred between day "0" (the last determination prior to the event) and day "3" (immediately following the event). "A" and "U" prefixes in legend designate Aquod and Uadult, respectively. Piezometric heads in the upper sandy zones for both soils decreased more rapidly after the rain event than did the argillitic horizons resulting in artesian-like conditions in the argillitic horizons.

The argillic is common to both soils, but its upper boundary is slightly shallower in the Uduft (Fig.3-1, Table 3-1). Also, the clay content of the upper part of the horizon is greater for the Uduft (Table 3-1, and replicate data not shown). Possibly, lower hydraulic conductivity (Table 3-2) associated with higher clay content in the Uduft argillic is a factor in maintaining a lower piezometric head than that within the argillic of the Aquod. However, a similar abrupt piezometric head drop has been documented at a site where the argillic texture and upper boundary depth were nearly constant for the Aquod and Uduft (Garman et al., 1981). The fact that hydraulic heads measured below the zone of podzolization (Bh) show close spatial correspondence to the presence or absence of Aquods is significant, regardless of the specific nature of the hydrological system. Podzolization processes, which are largely restricted to sandy materials (Brasfield et al., 1973; Holzhey et al., 1975; McKeague et al., 1983), are in this case (and in the case of the study of Garman et al., 1981) quite sensitive to the endoaquic hydrological conditions of the underlying, finer-textured argillic horizon. Aquods without argillic horizons are common as well, which means that any hydrological system which maintains wet conditions within the sandy zones could promote podzolization within those zones if other factors (as yet, incompletely understood) are favorable.

The piezometric head of the Uduft argillic horizon was much slower in responding to a rainfall event (i.e., before and after the event) than were those of other horizons due to high hydraulic resistance (hydraulic resistance = $1/K_{sat}$). Thus, the watertable in the upper sandy horizons of the Uduft can be temporarily epiaquic (perched), but subsequently regains endoaquic status probably because of continuous infiltration from

the upper horizons and upward water pressure of the argillic horizon. In effect, occurrence of near-surface saturated conditions in the Uduto eluvial horizons was restricted to relatively short intervals following rainfall. Conversely, near-surface saturation was maintained for longer periods in the sandy zone of the Aquod by the high piezometric head of the Btg (as described above). Epiaqueic conditions were rarely observed in the Aquod. In effect, the Aquod argillic showed a fast piezometric response to rainfall such that epiaqueic conditions were of very short duration. No incidence of a perched watertable above the Bh horizon was observed after a rainfall event.

The fact that the Bh horizon depth and intensity of expression increase with decreasing watertable depth shows that these factors are not simple functions of central tendencies in watertable dynamics. They are, at least for this study and for the study of Garman et al., (1981), related to duration of near-surface saturation within the sandy soil zone. The formation of E and Bh horizons entails a linked eluvial-illuvial process that apparently is triggered by threshold conditions attained with sufficient time of water saturation. In effect, saturation in some way promotes the destabilization and mobilization of components (i.e., dissolved organic carbon, fine colloids, etc.) that subsequently are redistributed to form the E - Bh sequence. The podzolic E horizon thickens in a surface-downward fashion along the transition, suggesting that destabilization and mobilization of the affected components progress to a diminishing degree with decreasing extent and duration of saturation to the point where they have not occurred at all (e.g., the Uduto).

Summary

The abrupt boundary (<5 m) between the Aquod and Udult soils corresponds to an abrupt hydrological change from relatively wetter to drier conditions. Depth and color development (low value) of the Aquod Bh horizon relate to duration of watertable in the near-surface sandy zone, but not to extremes or central tendencies in watertable depth. The Aquod argillic horizon was artesian with respect to its upper boundary. Hence, it is a temporary source of water to overlying sandy horizons, and serves to offset evapotranspiration loss during intervals between rainfall. In contrast, the Udult argillic was less commonly saturated in the upper part, and the overlying sandy horizons were unsaturated >50% of the time. The watertable slope across the Aquod-Udult boundary decreased to a minimal gradient during and shortly after periods of heavy rain, but increased during dry periods to eventually resume the gradient established between the adjoining argillic horizons of the two soils. The close correspondence between hydrological and morphological transitions further documents the association between water table, sandy texture, and podzolization within the region.

CHAPTER 4

GROUNDWATER COLLOIDS AS RELATED TO SOIL MORPHOLOGY AND GROUNDWATER DYNAMICS

Introduction

Colloids are ubiquitous in soils and aquatic systems. They are a factor in natural geochemical fluxes and have the potential to facilitate contaminant transport (Means and Wijayaratne, 1982; Orlandini et al., 1990; Sigleo and Means, 1990). However, little is known about the nature and abundance of in-situ colloids in groundwater, due to the difficulties of collecting valid samples and of characterization. This chapter addresses how the composition and concentration of groundwater colloids relate to hydrological- and soil morphological variables on the Florida flatwoods landscape described in Chapter 3.

Materials and Methods

Study Site

The study site has been described in Chapter 3.

Technique for Groundwater Sampling

It is critical that colloids not be artificially mobilized by perturbation resulting from sampling. However, avoiding artifacts in groundwater colloid investigation requires special sampling protocols. Therefore, besides the installation of the watertable monitoring piezometers described in Chapter 3, specific piezometers were separately installed for groundwater sampling in this study. They were designed and constructed to minimize disturbance during the installation and sampling steps, as described below.

Construction of piezometers for groundwater sampling

The design of the piezometer consisted of three parts: piezometer probe, extending PVC pipe, and sampling tube (Fig. 4-1).

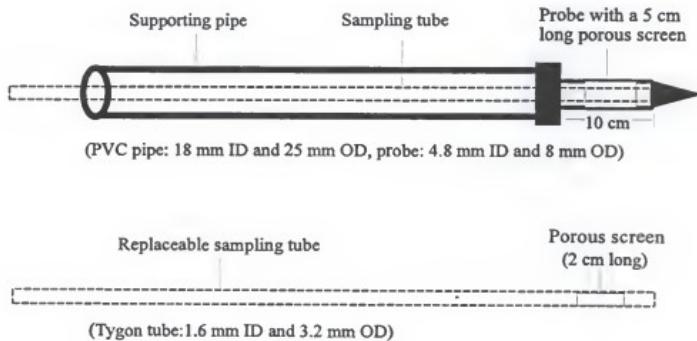


Fig. 4-1. Schematic of sampling piezometer with self-boring probe.

The piezometer probe was made of a 15-cm stainless steel tube with a diameter of 8 mm. Its bottom end was blocked and shaped into a conical tip so as to reduce self-boring resistance. The area serving as a screen was full of upward-angled holes, designed to minimize clogging by soil materials as the probe was pushed into the soil. A PVC pipe with an inside diameter of 2.5 cm was connected to the piezometer probe. A sampling tube with an inside diameter of 1.6 mm was used to avoid cross contamination while sampling and to permit control of pumping velocity. The inlet portion of the sampling tube was made like a porous screen whose length was about 2 cm. Its bottom was blocked. The outlet protruded from the top of piezometer body.

Piezometer installation for groundwater sampling

The placement of groundwater sampling piezometers across the field site (Fig. 3-2) followed a randomized block design (Table 4-1). The installation procedure can be summarized as follows. First, a hole of 4.0 cm in diameter was pre-drilled down to the top of the horizon where the piezometer's screen was to be positioned. Then, the piezometer was placed into the bigger PVC pipe (4.0 cm OD) and directly driven from the center of the bottom of the pre-drilled upper hole into the target horizon. A core was taken to make sure that the joint of both PVC pipe and piezometer probe were in tight contact with the top of the horizon being sampled in order to prevent "short circuits" of water flow. The depth of the piezometer screen was dictated by soil horizon depth.

Table 4-1. Piezometer placement for groundwater sampling (randomized block design).

Soil		Aquod			Udult		
Block		1	2	3	1	2	3
Treatment (Horizon where Piezometer was installed)	Btg	Bh	Btg	Bt	E	EB	
	E'	E'	Bh	EB	EB	Bt	
	Bh	Btg	E'	E	Bt	E	

Groundwater sampling protocol

The sampling procedure was designed to minimize artificial release of colloids and to obtain samples representative of the in-situ water chemistry conditions.

Groundwater was withdrawn by pumping slowly from piezometers. Purge was accomplished through a permanently installed separate tube, so as not to leave a contaminating residue. The method of prolonged slow pumping at a steady rate, proposed by Backhus et al. (1993), was adopted and further adjusted for piezometer effluent samples based on hydraulic conductivities of target horizons.

A type of mini-suction lift pump was applied in this study because the groundwater tables in the study sites are much less than 6 meter (Nielsen and Yeates, 1985) from the ground surface, and no volatile and gas-sensitive analytes were involved. Intervening glass reservoirs prevented any direct contact of the water sample and the pump interior. The pump was powered by a rechargeable battery. Pumping rate was adjusted by a stopcock connected with sampling tube. The groundwater was directly pumped into a glass container. Disturbance of screened water would be eliminated by the

Table 4-2. Description of sampling process and quality control.

Components of sampling protocol	Process description and requirements
<i>Sampling date and frequency</i>	Groundwater was usually sampled from every piezometer on Thursday or Friday based on a bi-weekly schedule. Unscheduled sampling was also conducted following rainfall events to get water from shallower piezometers which were usually dry at scheduled times.
<i>Sampling duration</i>	From May, 1997 through January, 1998.
<i>Pump</i>	A mini suction lift pump (Barnant Model B3041, Barnant Corp.)
<i>Pumping rate</i>	5-20 mL min ⁻¹ , depending on hydraulic conductivities of target horizons; about 5 mL min ⁻¹ for Bt/Btg horizons, 10 mL min ⁻¹ for Bh and EB horizons; and 20 mL min ⁻¹ for E and E' horizons. The establishment of these constant pumping rates was to minimize artificial release of colloids. Pumping rate was controlled by the stopcock connected to sampling tube.
<i>Pumping system</i>	Pumping system consisted of a pump, a rechargeable battery (12 V), a glass bottle for vacuum, three water sample collectors and tubes.
<i>Sample containers and identification</i>	1000 mL polyethylene bottles were used as water containers. Sample containers were labeled with piezometer numbers and date.
<i>Sample volume</i>	Dependent on individual piezometer (up to 2000 mL).
<i>Sample storage</i>	Samples were immediately placed in a large ice chest at the site, and in a refrigerator after being transported to the laboratory.
<i>Partitioning of water samples</i>	From each fresh groundwater sample, three subsamples of about 20 mL water were first partitioned into 25 mL polyethylene bottles for organic C analysis, pH and EC measurements, and particle size distribution. When needed, another 60 mL was withdrawn to measure total solid mass. The remainder was kept and accumulated for mineralogical analysis.

permanently installed sampling tube (Fig. 4-1). The volume of sample was dictated by the requirements for total solid and organic C (including DOC) analysis, and mineralogical analysis via X-ray diffraction, which was pre-determined by preliminary study. Details of sampling protocol are presented in Table 4-2.

Analyses of Groundwater Samples

Chemical, physical, and mineralogical characterization of groundwater samples, from different horizons and under changing hydrological conditions, were performed.

Measurements of pH and electrical conductivity

Measurements of pH (pH meter 240, Corning) and electric conductivity (EC in $\mu\text{mho cm}^{-1}$) (Markson EC meter, Model 1054) were performed shortly after samples were brought to the lab (usually within 12 h).

Determination of total mass via gravimetry

Total solid concentration (TS) (including dissolved solutes) was determined for all samples. A precise 20 mL aliquot was withdrawn in triplicate from sample container by pipette, deposited in tarred weighing pans, and placed in an oven to dry at 45 °C. Pans were then removed from the oven when residues were dry, covered, and allowed to equilibrate in a desiccator at 56% humidity [$\text{Mg}(\text{NO}_3)_2$ solution]. Residue weight was then determined on a 5-place electronic microbalance. From this weight and the aliquot volume, total entrained concentration was calculated.

Determination of > 0.2 μm colloidal retentate

Samples were filtered using a 0.2 μm PTFE membrane by means of a suction pump. The first 100 mL filtrate was discarded to reduce possible contamination (mainly OC) from the filter membrane, after which about 150 mL filtrate was collected for other analyses. After filtration, the retentate was saturated with 1 N MgCl₂ and free salt was rinsed with de-ionized water, in preparation for mineralogical analysis. The filter with retentate was then placed in a desiccator at 56% humidity for mass determination and mineralogical analyses. The solute mass in the filtrate was determined in the same way as described in the section of "Determination of total mass via gravimetry". The difference between the TS concentration in raw water and the total solute mass in the filtrate constitutes an estimate (mg L⁻¹) of colloids > 0.2 μm in size, though smaller colloids could have been trapped in the filter cake as well.

Determination of total-, organic-, and inorganic Carbon

Total carbon (TC), inorganic carbon (IC), and organic carbon (OC) (Nelson and Sommers, 1982) was determined using a carbon analyzer (TOC-5050 Shimadzu Corporation) for samples collected bi-weekly from all piezometers containing water. The instrument is based on the combustion/non-dispersive infrared gas analysis method. Analyses were conducted in duplicate for both unfiltered and filtered (0.2 μm) groundwater samples.

UV-visible absorbance of water samples at wavelength of 665, 465, and 254 nm was measured using a UV-Visible Recording Spectrophotometer (UV 160U, Shimadzu) (Traina et al., 1990).

Determination of inorganic composition of colloids

Particles collected using a 0.2 μm filter (retentate) were used for solid-state assessments, including X-ray diffraction (Whittig and Allardice, 1986) and scanning electron microscopy (SEM).

Isolation and pretreatment of materials. The > 0.2 μm retentate was saturated (while still on the filter) with magnesium by washing with 1 N MgCl₂ followed by deionized water (to remove free salt). This was done to establish a standard condition for identification of expandable phyllosilicates by X-ray diffraction (Whittig and Allardice, 1986), should they be present. Glycerol solvation of the Mg-saturated material and/or K-saturation with heat treatments were used when needed for unequivocal identification. The pre-saturated retentate was gently removed from the filter using a rubber-policeman, transferred to a glass slide, allowed to dry, and weighed. It was then stored for subsequent analyses.

X-ray-diffraction (XRD) analysis. Mounts for XRD were prepared by transferring the retentate to a specially cut quartz crystal surface which minimizes background scattering. Samples were scanned at 2° 2 θ per minute using CuK α radiation. Scans were conducted at 25 °C for Mg-saturated samples. Minerals were identified from XRD peak positions, making use of differentiating responses to saturation and heat treatments (Whittig and Allardice, 1986).

The quantitative determination of soluble inorganic constituents (such as Al, Fe, Si, Ca, Mg, K, Na, etc.) was conducted on the water samples using inductively-coupled plasma (ICP) analyses.

Readily-Dispersible Colloids (RDC)

Traditionally, the percentage of clay determined by mechanical means without removing aggregating agents or the use of a chemical dispersant is referred as *water dispersible clay* (WDC) (Burt et al., 1993). Much effort has been directed toward development of a method by which the water-dispersible colloids can be accurately assessed, so as to reflect erodibility of surface soil due to rain events. The term *readily-dispersible colloids* (RDC) will be used in this chapter to designate colloids that would most likely be entrained in pore water and transported by groundwater flow (Curtin et al., 1994).

In order to elucidate the relationship between the characteristics of colloids suspended in groundwater and the RDC in the soil matrix, intact soil samples were taken to obtain the natural readily-dispersible colloids by gently shaking with rain water.

Sampling of intact soil cores

A probe with an internal diameter of 3 cm was used to obtain intact soil cores in the vicinity of the piezometer from which groundwater was sampled. All soil cores were kept in a refrigerator prior to analysis.

Dispersion procedure

Readily-dispersible colloids. A 100 g fresh soil core sample was placed in 1000 mL glass cylinder (soil samples from Bt and Btg horizons were coherent and required gentle separation) and the rainwater (collected from the campus with pH of 6.5 and EC of 11 $\mu\text{mho cm}^{-1}$) was gently poured down the inside of the cylinder to saturate the soil

for one hour. Then, the cylinder was brought up to 1000 mL volume by slowly adding rainwater, and was very slowly inverted for 30 seconds (about three times) before being placed upright. This was intended to produce a homogeneous suspension with minimal disturbance of soil aggregates (Curtin et al., 1994). The beginning time was immediately recorded. The suspension was allowed to stand in a 22 °C waterbath for the required settling time, which was calculated using the Stoke's law for < 1.0 μm colloid suspension at a 15 cm depth. Afterwards, using a 200 mL automatic pipette, an aliquot was drawn at the required time. A blank using rainwater only was set for each run. The water content of the fresh soil sample was determined gravimetrically.

pH10 water-dispersible colloids. A 50 g fresh soil sample (25 g for Bt and Btg horizon samples) was placed into a 250 mL glass beaker and 100 mL pH10 water was added to the beaker. A rubber policeman was used to help separate aggregates. The suspension was completely transferred to a mixer cup and mixed for 3 minutes. Then the sample was completely transferred from the cup to a glass cylinder and brought to 1000 mL with pH10 water, sealed and shaken, and placed in a 22 °C water bath. The remaining steps were as described above for the readily-dispersible colloid determination.

Partition and determination of suspension samples

A 10 mL sub-aliquot of RDC and pH10 water-dispersible colloid suspensions was withdrawn by pipette for residue measurement in duplicate. Two additional 10 mL sub-aliquots were saved for analysis of OC and particle size distribution respectively. The rest of the suspension was fractionated using a 0.2 μm filter membrane. Retentate on the filter was saturated with 1 N MgCl₂ and saved for mineralogical analysis, and the filtrate was

saved for DOC analysis. The procedures for all variable determinations were the same as those used for groundwater samples.

Analysis of Colloid Size Distribution

Principles of ultrafine particle size analysis

The underlying principles of this technique relate to dynamic light scattering. According to Brownian motion theory, particles suspended in a dispersing fluid are subject to random collisions between them and thermally excited molecules of the fluid (Chu, 1991; Pecora, 1985). The velocity and direction of the resulting motion are random, but the velocity distribution of a large number of monosized particles averaged over a long time will approach a known functional form. Generally, the velocity of particle motion is inversely proportional both to the particle size and fluid viscosity. Also, light incident to a particle scatters in all directions. If the particle is stationary, the scattered light is of the same frequency as the incident light. If the particle is moving at some velocity relative to the light source, the scattered light is shifted in frequency by an amount proportional to the particle velocity. An ensemble of particles with a certain velocity distribution will thus have a unique distribution of frequency shifts. That is called the Doppler effect. The frequency spectrum is uniquely determined by the particle velocity distribution which in turn is uniquely determined by the particle size distribution. The particle size distribution is computed directly from the measured frequency spectrum recovered from the Doppler-shifted scattered light.

Parameters and conditions

The ultrafine particle-size analyzer (Microtrac-UPA150) used for this study is an independent optical measuring device that gathers and transmits data to a computer for necessary computations. It is designed for process monitoring and control for particle mixtures in the size range of 3.2 nm to 6.541 μm , which was subdivided into 44 channels (sub size-range intervals). It was assumed that colloids suspended in groundwater are dominated by irregularly-shaped siliceous component with a refractive index of 1.54. Run time was set at 180 seconds, and the results were the average of two consecutive runs and expressed either in particle number distribution or particle volume distribution.

Statistical Analysis

All data were analyzed using SAS and T tests (LSD -- Least Significant Difference) were applied for variable comparisons.

Results and Discussions

Colloid Characteristics as Related to Soil Morphology

pH and electrical conductivity (EC) of groundwater

As addressed in Chapter 2, pH and ionic strength could be determinant factors responsible for the dispersion and mobilization of colloids.

Groundwater samples from all Aquod piezometers at different sampling dates had an average pH value of 4.4 (± 0.3) with a 6.8% variation, while the average for Udult samples was 5.2 (± 0.4) with a variation of 7.7%. The difference in groundwater pH between the Aquod and Udult was statistically significant ($p < 0.0001$, $n = 120$). Such differences between horizons within each soil (Fig. 4-2) were also statistically significant. The pH of groundwater sampled from the Aquod E horizon was about 0.5 unit lower than other Aquod horizons ($p < 0.001$, $n = 72$), and spatial variation (block effects) was negligible. Within the Udult, differences were noted between E and EB, and BE and Bt ($p < 0.05$, $n = 48$), which includes significant contribution from block effects. The lower pH of the Aquod groundwater may be due to greater activity of organic acids (see next section).

Variations with sampling date (Fig. 4-3 and 4-4) could be attributed to the intensity and frequency of rainwater infiltration through sampling zones. Sampling was not frequent enough to assess the relation between pH value and precipitation. However, the pH (6.5) of rainfall was usually about 2 units higher than those of both soil matrices,

so a pH influence from rainfall seems likely (e.g., the overall average pH value of groundwater is 0.3 unit higher than that of soil matrix in the Udult area) (Table 4-3).

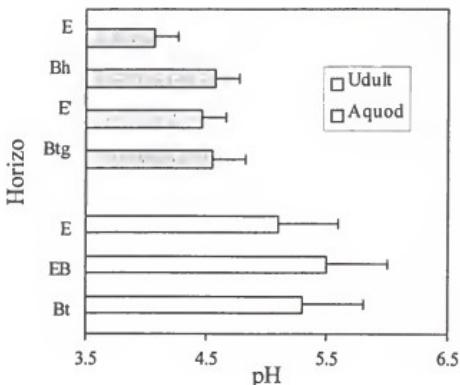


Fig. 4-2. Mean values of groundwater pH for specified horizons of the Aquod and Udult (showing one standard deviation, n=17).

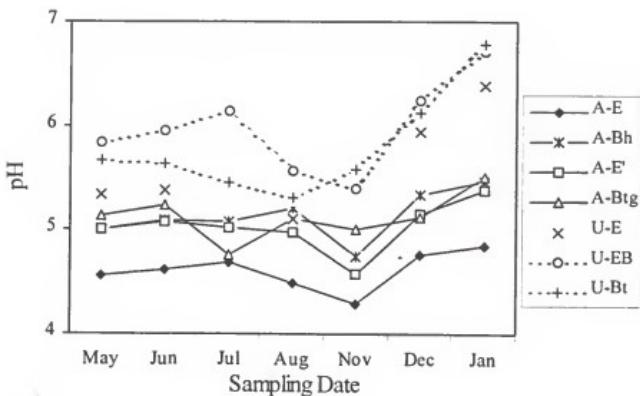


Fig. 4-3. Variation of groundwater pH over time within the Aquod (A) and Udult (U) horizons.

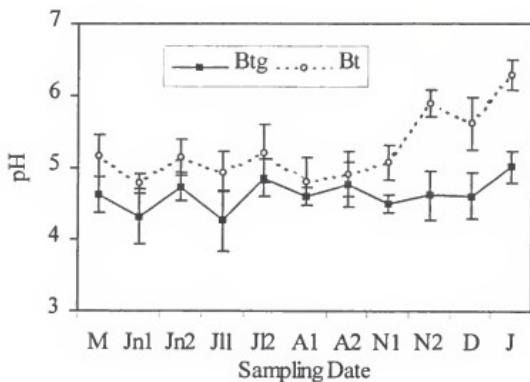


Fig. 4-4. Fluctuation of mean groundwater pH (variation indicated by mean ± 1 std.) within Aquod-Btg and Uduft-Bt horizons for the complete sampling period of this study.

Table 4-3. Selected properties of soil matrices corresponding to piezometer screens[†].

Soil	Horizon	Screen Interval (cm)	pH	EC umho cm ⁻¹	OC %	<1 μm clay (%)	Citrate-Dithonite Al (%)	Fe (%)
Aquod	Ap [‡]	0-18	3.9	63	2.41			
	E	25-30	4.3	21	0.42	0.52	0.003	0.003
	Bh	35-40	4.5	56	2.41	1.23	0.321	0.014
	E'	64-69	4.6	34	0.36	1.18	0.057	0.045
	Btg	100-105	4.9	27	0.22	16.29	0.091	0.327
Uduft	Ap [‡]	0-10	4.5	54	1.67			
	E	25-30	4.8	38	0.24	2.25	0.059	0.092
	EB	41-46	5.0	24	0.27	10.41	0.063	0.184
	Bt	100-105	5.0	27	0.30	22.34	0.087	0.302

† Each of all data in the table is an average of triplicate.

‡ No piezometer installed.

EC (electrical conductivity) is proportional to total soluble inorganic components.

Generally, ECs of groundwater samples were very small, ranging from $49 \pm 9 \mu\text{mho cm}^{-1}$ in the Uduto to $66 \pm 8 \mu\text{mho cm}^{-1}$ in the Aquod (Fig. 4-5 and 4-6), which were much higher than those of corresponding soil matrices except for Ap horizons (comparing with Table 4-3). The difference between the two soils was significant ($p < 0.0001$, $n = 120$), with negligible block effects. Also, the Bh-horizon groundwater samples had significantly lower EC ($p < 0.01$, $n = 72$), and EC tends to increase with depth in the Uduto ($p < 0.01$, $n = 48$).

Higher groundwater EC in the Aquod, especially in the E horizon, was a significant but unexpected result. As addressed in Chapter 3, the Aquod had higher hydraulic conductivities and piezometric heads than did the Uduto. Possibly the Aquod area was enriched in soluble salts from surrounding areas. EC fluctuation with sampling date (Fig. 4-6) was much less pronounced in Btg and Bt horizons than in overlying sandy horizons, probably due to the lower hydraulic conductivities of the Btg and Bt zones.

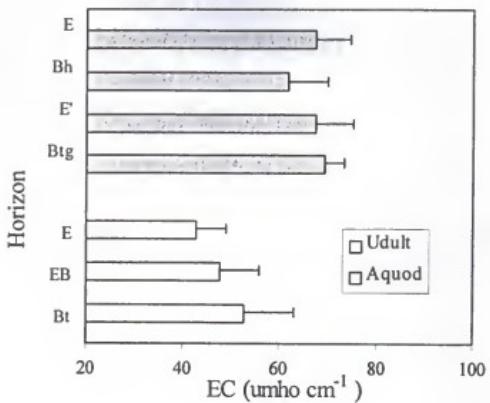


Fig. 4-5. Mean values of groundwater EC for specified horizons of the Aquod and Udult (showing one standard deviation, $n=17$).

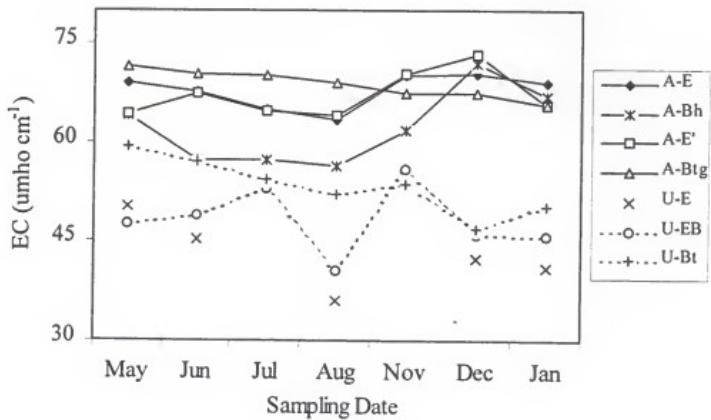


Fig. 4-6. Variation of groundwater EC within the Aquod (A) and Udult (U) with sampling date.

TS and OC in groundwater

The spatial and seasonal variations in TS (Fig. 4-7 and 4-8) showed that:

- (1) On the average, TS for the Aquod horizons ($60.0 \pm 10.7 \text{ mg L}^{-1}$) were much higher than those for the Uadult horizons ($30.6 \pm 9.5 \text{ mg L}^{-1}$) ($p < 0.001$, $n = 120$).
- (2) Within the Aquod, TS decreased significantly with depth ($p < 0.001$).
- (3) TS concentrations varied significantly ($p < 0.01$) with sampling date for all horizons except for the Bh and E' of the Aquod (Fig. 4-8).

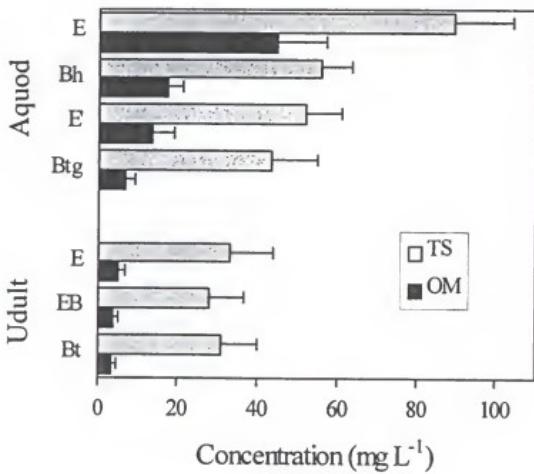


Fig. 4-7. Mean values of groundwater TS and OM ($\text{OM} = \text{OC} \times 1.724$) for specified horizons of the Aquod and Uadult (showing one standard deviation, $n = 17$).

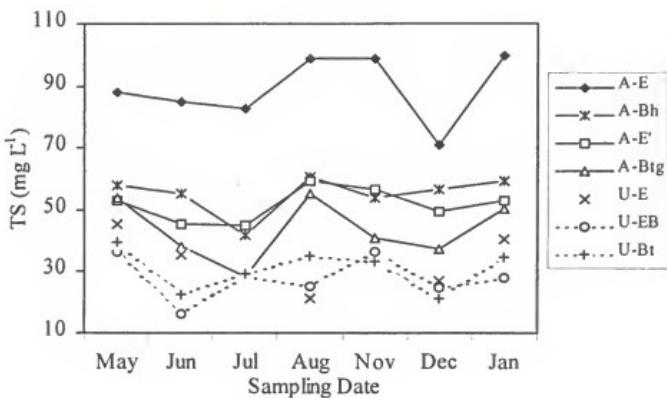


Fig. 4-8. Variation of groundwater TS with sampling date within the Aquod (A) and the Udult (U).

OC concentrations in groundwater showed that organic matters (OM) make up a greater fraction of TS in the Aquod area than in the Udult area (Fig. 4-7), with an average range from $20.7 \pm 6.0 \text{ mg L}^{-1}$ for the Aquod to $4.1 \pm 1.4 \text{ mg L}^{-1}$ for the Udult. The magnitude varied much more with depth in the Aquod, for which all horizons tested significantly different from each other ($p < 0.001$, $n = 108$). However, soil spatial variability (block effect) contributed significantly to this variation, possibly due to rotting roots. Variation of OC with sampling date was greater for the Aquod E horizon (Fig. 4-9). Generally, statistical analysis showed a remarkable spatial variability, especially for sandy horizons. In contrast to TS, however, OC concentration in the Btg and Bt horizons remained relatively constant with sampling date (Fig. 4-10). The variation in TS for the latter horizons appears to derive mainly from fluctuation of colloid concentration, since EC values do not indicate much temporal change in soluble components.

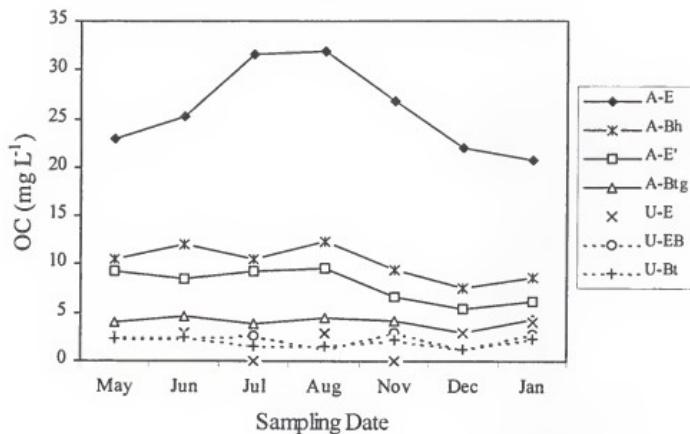


Fig. 4-9. Variation of groundwater OC with sampling date within the Aquod (A) and Udult (U).

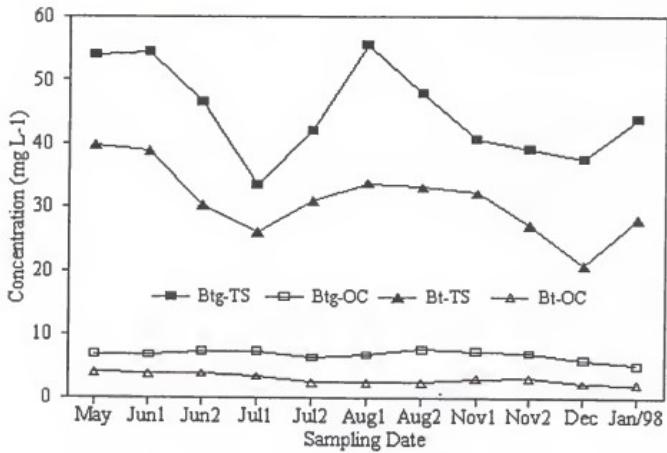


Fig. 4-10. Variation of groundwater TS and OC in Aquod-Btg and Udult-Bt horizons during a period from 05/97 through 01/98. No water was obtainable in September and October. The number "2" designates the second sampling interval for the indicated month.

Colloids retained on 0.2 μm filter

A 0.2 μm filter membrane was used to collect colloids for mineralogical analysis (Table 4-4). The concentration of > 0.2 μm diameter colloids suspended in groundwater can be inferred to be low, since the average of > 0.2 μm retentate (which could also contain some finer particles) concentration ranged from $3.4 \pm 2.2 \text{ mg L}^{-1}$ in the Aquod to $2.1 \pm 1.1 \text{ mg L}^{-1}$ in the Uduft. This constitutes 5.6% and 7.6% of TS, respectively.

Table 4-4. Concentration of groundwater colloids retained by > 0.2 μm filter.

Soil	Sampling Date Horizon	May	Jun	Aug	Dec	Avg	Std	P/TS [†]
		mg L ⁻¹						%
Aquod	E	2.5	3.3	2.0	.	2.6	1.8	4.0
	BH	3.8	6.5	3.8	1.3	4.1	2.0	7.1
	E'	3.6	4.5	2.7	1.9	3.2	2.0	6.2
	Btg	3.0	4.4	2.4	1.7	2.9	1.5	6.3
Uduft	E	2.0	4.2	2.1	2.4	2.7	1.2	8.4
	EB	2.1	2.4	1.6	1.2	1.9	1.0	4.7
	Bt	1.0	.	1.2	.	1.1	0.3	3.7

† Percentage of > 0.2 μm colloids in total solids (< 1 μm).

Soluble inorganic components in groundwater

The average amount of all detected soluble cations in groundwater ranged from 8 ppm for the Uduft to 12 mg L⁻¹ for the Aquod (Table 4-5). Sodium was most abundant, followed by Ca and Si. Soluble Al and Fe contents in groundwater were much higher in the Aquod than in the Uduft. Longer periods of wetness in the Aquod area than in the Uduft area would tend to solubilize Fe via chemical reduction. Also, the Aquod groundwater was richer in organic components, which could favor complexation of Al.

SEM analysis (crystal morphology and elemental composition by energy-dispersive X-ray spectroscopy) verified the presence of NaCl in the residue of raw groundwater (Fig. 4-11).

Table 4-5. Soluble inorganic cation concentrations (mg L^{-1}) in groundwater.

Soil	Horizon	Na	Ca	Mg	K	Al	Fe	Si	Total	Std
Aquod	E	4.3	2.2	1.0	0.3	0.8	0.2	1.7	10.4	2.1
	Bh	5.0	1.6	0.8	0.0	0.6	2.0	1.1	11.0	1.2
	E'	5.7	0.9	0.8	0.0	0.4	3.8	1.6	13.2	2.4
	Btg	6.7	1.1	1.0	0.0	0.1	2.7	1.6	13.1	0.5
Udult	E	2.3	1.3	0.6	0.0	0.2	0.0	2.0	6.4	0.7
	EB	3.9	1.6	1.0	0.0	0.1	0.0	1.2	7.9	1.7
	Bt	7.3	0.7	1.1	0.0	0.0	0.0	1.4	10.6	1.8

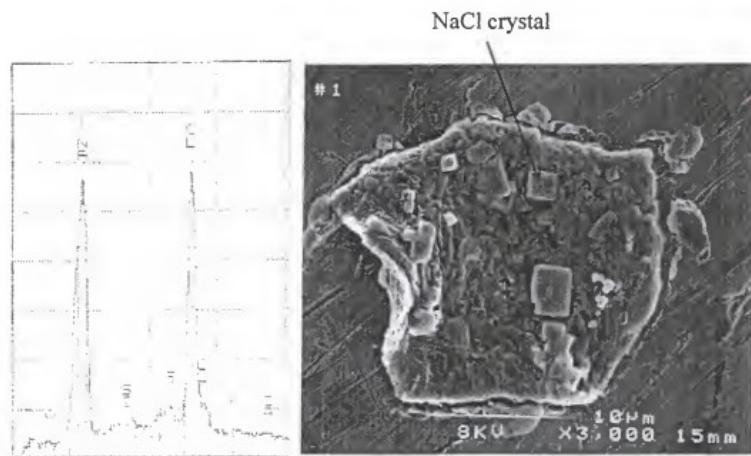


Fig. 4-11. Elemental spectrum produced by energy-dispersive X-ray analysis (left) and SEM image (right) of aggregates formed during the drying of a groundwater sample from the Aquod-Btg horizon.

Components of TS in groundwater can be classified as organic and inorganic, or as colloidal and dissolved. Distinction between colloidal and dissolved components of TS is hindered by the practical difficulty of physically separating colloids at the lower cut-off limit, as well as by the fact that the distinction between "colloid" and "molecule" is not distinct for organic components. For the purpose of this study, the colloid vs. solute distinction will be operationally defined as the difference between TS and total soluble inorganic components as determined above. All organic components will be considered as colloids, based on the lower size limit of 1 nm (equivalent to a molecule weight cutoff --1000 daltons), which is likely exceeded by most organic molecules in groundwater (Kwak et al., 1977; Stevenson, 1982). Inorganic colloids, by this convention, would be defined as the difference between total colloids and organic colloids. Composition of TS, based on these distinctions, varied greatly with soil (Aquod vs. Udult) and soil horizons (Table 4-6 and Fig. 4-12). Organic colloids in both concentration and proportion of TS, decreased significantly with depth for the Aquod, but a decrease only occurred between the E and EB horizons for the Udult. Roughly, total colloid contents of shallower groundwater in the study area (except for the groundwater samples taken from the Aquod E horizon) fall in and tend to approach the higher limit of the colloid concentration range drawn from other groundwater studies (Fig. 4-13).

Table 4-6. Components and their relative proportions of groundwater solids.

Soil	Horizon	TS	Soluble Inorg. Components [†]	Total Colloids		> 0.2 μm Colloids [‡]
				Organic	Inorganic	
			mg L ⁻¹			
Aquod	E	99	27	55	17	2.7
	Bh	61	27	22	12	3.7
	E'	59	30	18	12	2.4
Udult	Btg	57	31	9	17	2.5
	E	22	14	5	3	2.0
	EB	26	21	2	3	1.2
	Bt	36	28	3	5	1.1

† Calculated by assuming that Na, Ca, Mg, and K present in the form of chlorides and Al, Si, and Fe as oxides.

‡ Retained on 0.2 μm filter and including organic and inorganic colloids.

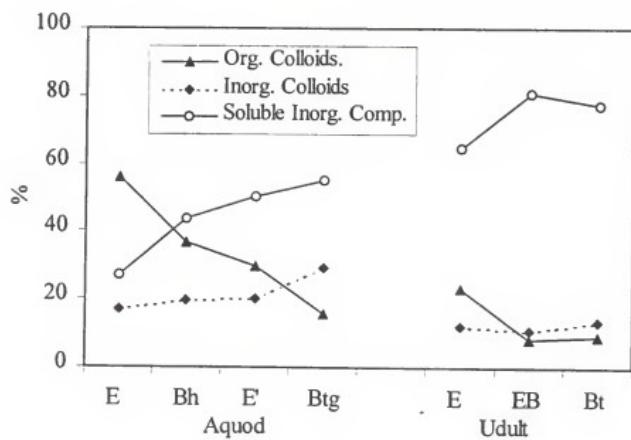


Fig. 4-12. Relative proportions of organic- and inorganic colloids and soluble inorganic components in groundwater sampled from designated horizons on 08/02/97 (Taking TS as 100%).

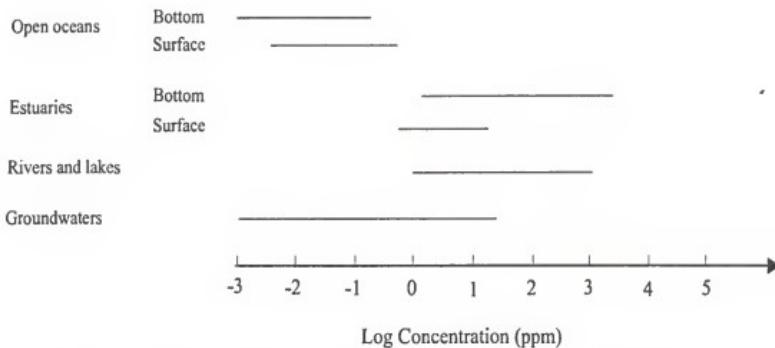


Fig. 4-13. Mass concentration ranges of colloids in various aquatic systems (references as listed in Table 2-1).

Compositional Differences of Colloids between Groundwater and Soil Matrices

Fractions of organic and inorganic components

Some differences are evident between groundwater and the soil matrix from which it was collected with respect to solid components (Table 4-7):

- (1) TS suspended in groundwater was very dilute and not proportional to the amount of readily-dispersible colloids (RDC) released from soil matrix. In effect, groundwater TS does not necessarily correspond to the relative dispersibility of soil matrices.
- (2) The fraction of OC passing the $0.2 \mu\text{m}$ filter (designating OC passing the $0.2 \mu\text{m}$ filter as DOC as shown in Table 4-7) varied with soil types and horizons: this fraction dominated in EB and Bt horizons of the Ultisol, while it was a small part of OC in other

Table 4-7. Dispersible components in soil matrices and groundwater.

Soil	Horizon	Soil matrices				Groundwater [†]			
		TD ¹ %	RDC ² mg kg ⁻¹	OC ³ mg kg ⁻¹	DOC/OC ⁴ %	OM/RDC ⁵ %	TS mg L ⁻¹	OC mg L ⁻¹	DOC/OC %
Aquod	E	0.5	666	119	20.1	31	99	31.8	93
	Bh	1.2	6595	1399	4.5	37	61	12.4	82
	E'	1.2	2440	327	8.8	23	59	9.7	91
	Btg	16.3	7962	133	17.7	3	57	4.4	88
Udult	E	2.2	3858	106	21.5	5	20	3.9	86
	EB	10.4	624	24	71.3	7	26	1.2	62
	Bt	22.3	709	22	80.1	6	36	1.5	50

[†] Groundwater samples were taken on August 2, 1997.1 <1 μm total colloids dispersed by pH10 water which includes organic components.2 <1 μm colloids dispersed by rainwater which includes organic components.

3 Total organic carbon entrained in readily-dispersible colloids.

4 Percentage of OC passing 0.2 μm filter in total OC.

5 Percentage of dispersible organic components in readily-dispersible colloids (RDC).

6 Percentage of total organic components in total groundwater solid mass (TS).

horizons, especially in the Bh and E'. However, OC consisted mainly of DOC in groundwater, even for samples collected from horizons with an appreciable proportion of coarse particulate C (low DOC/OC in soil matrices; Table 4-7).

(3) The rapid OC decrease in groundwater from upper horizons to deeper ones was consistent with its origination from organic matter decomposition near the surface.

The OC concentration was particularly high in groundwater from the Aquod E horizon, which had very low clay content. Possibly, the very low adsorption capacity of this horizon resulted in minimal C being removed from groundwater, whereas the subjacent Bh horizon and the E horizon of the Uduto (both of which are relatively shallow) have sufficient reactive surface area to significantly reduce solution activity of C. The E - over - Bh horizon sequence constitutes an abrupt contrast between C and Al depletion (E) and C and Al enrichment. According to classical podzolization theory, this sequence developed via pedogenic complexation of Al by organic acids, vertical migration of the complexes, and subsequent precipitation of Al and C to form the Bh (McKeague et al., 1983). The present study suggested that C accumulation may be an ongoing process after the formation of the Bh horizon, which would help to explain why the C/Al ratio tends to be significantly higher in the upper Bh (Bh_1) of Florida Spodosols (Harris, 1998). The ratio of OC/TS in groundwater was higher than that of OC/RDC in soil matrices for all horizons but the Bh where soil OC was much higher than other horizons (Fig. 4-14). The higher proportion of C in groundwater solids than soil matrix colloids further supports the idea that OC is entrained in groundwater and originates from surface or surrounding areas.

Organic components transported within soils can play an important role in soil development (Dawson et al., 1978). The mobile organics within Spodosols have been found to be chemically similar to fulvic acid fraction or its precursors (Dawson et al., 1978; McDowell and Wood, 1984). Also, UV analysis of groundwater showed that both OC and DOC are particularly sensitive to the short wavelengths of 254 nm (Fig. 4-15), which has been reported by Amrhein et al. (1993) and Dunnivant et al. (1992). These data suggested that mobile organic components in the flatwoods soils of the study area could be mainly fulvic acids, especially within the deeper sampling zone, because fulvic acid has a higher ccharge density than humic acid (Stevenson, 1982) and therefore is potentially more mobile.

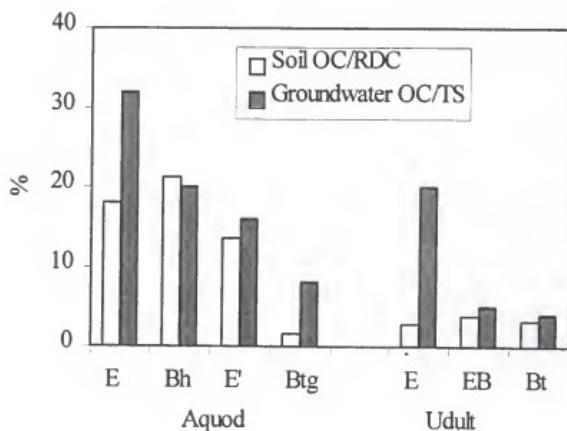


Fig. 4-14. Relative proportion of OC in soil readily-dispersible colloids (RDC) and in groundwater TS.

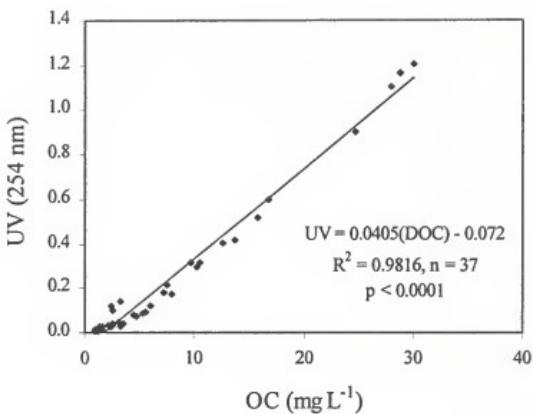


Fig. 4-15. Correlation of ultraviolet (UV) absorbance with OC in groundwater.

Colloid mineralogy

Data presented in the previous section showed that inorganic colloids comprised a significant proportion of TS in groundwater. Interestingly, mineralogical composition of groundwater colloids was very different from that of the soil matrix (Table 4-8; Fig. 4-16), as summarized below.

(1) Quartz, kaolinite, and some hydroxy-interlayered minerals (HIM) were detected in the RDC from sandy horizons of both soils, though quartz was more prevalent in the Aquod. Also, kaolinite dominated the clay fraction of the argillic horizons (Btg and Bt) of both soils, regardless of the means of dispersion.

Table 4-8. XRD index values (%) calculated from relative peak areas for minerals detected in RDC and pH10 water dispersible colloids[†].

Soil	Horizon	Blk	GW (8/2) [‡]			GW (12/1) [‡]			RDC			pH10		
			HIM	Kaol.	Qtz.	HIM	Kaol.	Qtz.	HIM	Kaol.	Qtz.	HIM	Kaol.	Qtz.
Aquod	E	1	0	0	100	0	0	0	3	15	82	1	18	81
	E	2	0	1	99	0	0	0	5	12	83	5	21	74
	E	3	0	0	100	0	0	0	3	17	80	1	17	82
	Bh	1	0	0	100	0	0	100	5	33	62	4	40	56
	Bh	2	0	0	100	0	0	0	3	40	57	3	41	56
	Bh	3	0	0	100	0	0	0	3	49	54	0	57	53
	E'	1	0	0	100	0	0	100	2	30	68	5	44	51
	E'	2	0	0	100	0	0	100	4	43	53	5	45	50
	E'	3	0	0	100	0	0	100	5	70	25	5	81	14
	Btg	1	1	30	69	0	0	100	8	89	3	5	93	2
Udult	Btg	2				0	1	99	3	97	0	2	98	0
	Btg	3	2	5	94	0	0	100	3	97	0	4	96	0
	E	1	0	11	89				3	76	21	3	85	12
	E	2	0	18	82				5	79	16	3	85	12
	E	3	2	18	80				5	70	25	5	78	17
	EB	1	0	16	84	0	8	92	4	51	45	4	85	12
	EB	2	4	24	72				3	82	16	2	98	0
	EB	3	0	24	76	0	0	100	3	78	19	2	91	7
	Bt	1								100	0	2	98	0
	Bt	2	0	14	86					100	0	2	98	0
	Bt	3	0	0	100					100	0	2	99	0

†: XRD index (%) of each mineral is calculated according to the areas of major XRD peaks normalized to 100% for all detectable minerals in the <1 µm groundwater colloids, rainwater dispersible colloids, and pH10-water dispersible colloids, respectively. The index reflects relative changes in mineral proportions from sample to sample, but is not equivalent to absolute mass percent.

‡: sampling date.

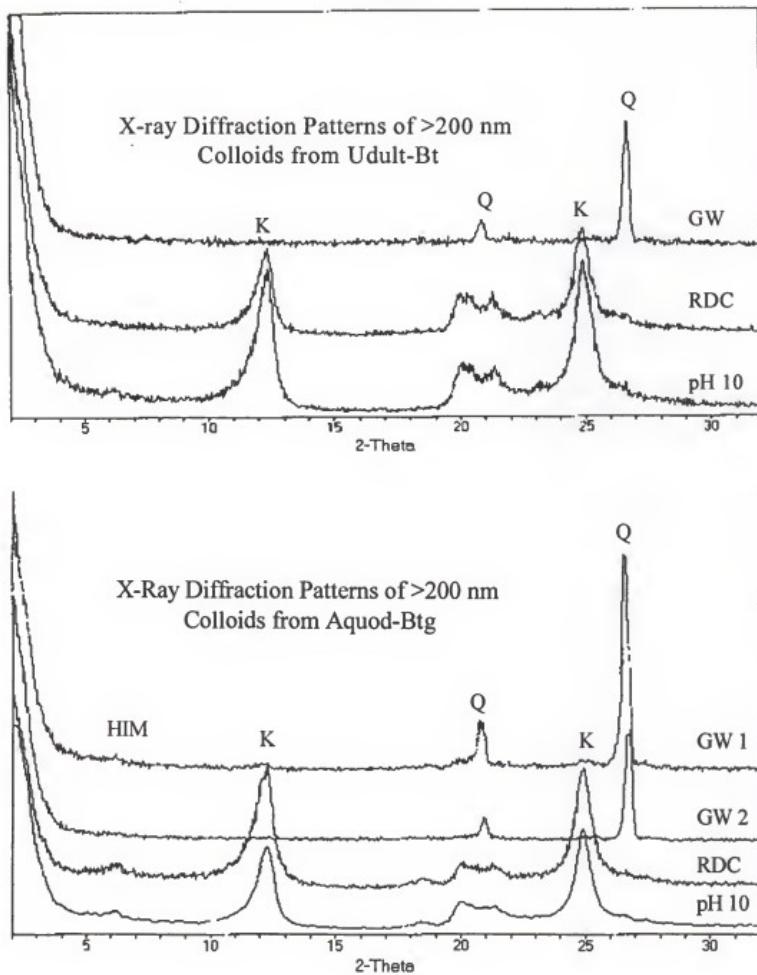


Fig. 4-16. X-ray diffraction pattern comparisons of colloids in groundwater and soil matrix from the Aquod and Udult areas. Mineral designations for XRD peaks are: HIM = hydroxy-interlayered minerals, K = kaolinite, Q = quartz. RDC = readily-dispersible colloids, pH10 = pH10 water-dispersible colloids, and GW = groundwater colloids.

(2) Groundwater colloids were predominantly quartz, even for samples from Btg and Bt horizons whose corresponding soil matrices had little or no quartz detectable in RDC and pH10 water-dispersible colloids (Table 4-8). Energy-dispersive X-ray elemental analysis conducted in conjunction with SEM (Fig. 4-17) confirmed the dominance of Si in groundwater colloids, and hence corroborated the XRD-based conclusion of quartz dominance.

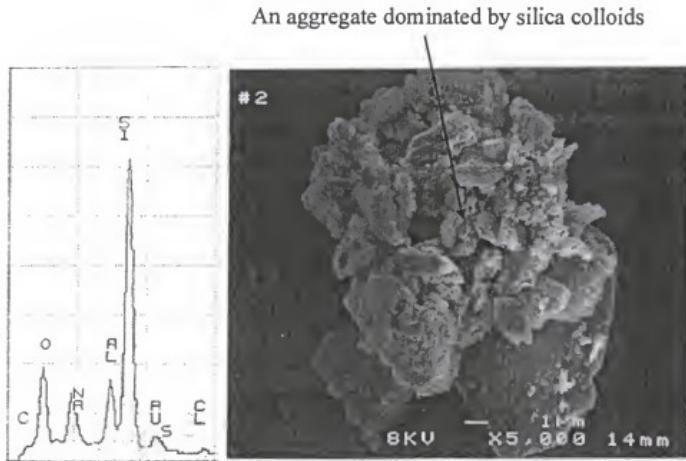


Fig. 4-17. Elemental spectrum produced by energy-dispersive X-ray analysis (left) and SEM image (right) of an aggregate formed during the drying of the >0.2 μm retentate of a groundwater sample from the Aquod-Btg horizon.

(3) The proportion of quartz was small but significantly higher ($p < 0.05$) in RDC than in pH10 water-dispersible colloids (by an average of 6% in the Aquod and 14% in Udult). The relative proportion of colloidal quartz decreased to near zero with depth for the Aquod matrix, but remained dominant with depth for the Aquod groundwater (Table 4-8; Fig. 4-17 and 4-18).

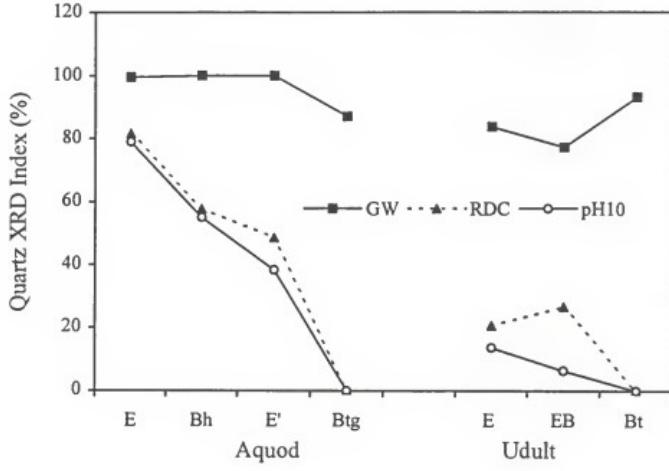


Fig. 4-18. Quartz XRD index[†] for colloids in groundwater (GW, $> 0.2 \mu\text{m}$), readily-dispersible colloids (RDC), and pH10 water-dispersible (pH10) colloids (1.0-0.2 μm) of samples collected from specified piezometers.

[†]: XRD index = $P_{\text{qt}}/\sqrt{(P_{\text{qt}} + P_{\text{him}} + P_{\text{k}})}$, where P_{qt} , P_{him} , P_{k} are XRD peak areas for quartz (3.34 Å), HIM (14 Å), and kaolinite (3.57 Å) reflections, respectively.

The difference in mineralogical composition between groundwater colloids and RDC from the soil matrix was statistically significant ($p < 0.0001$, $n = 20$). The higher proportion of quartz in RDC than in the pH10-water dispersible colloids within the Udult area suggested that quartz was the most dispersible and mobile mineral present in the colloid fractions of these soils under natural pH and EC conditions. The dominance of quartz in groundwater sampled from the zones in which the matrix colloids contained little or no quartz is evidence that the quartz was entrained and moving with the water.

The effect of pH on colloid mobilization may vary with the mineral composition of soil matrix. High pH will increase negative charge density on colloid surfaces and promote the release and transport of the colloids with low PZC (point of zero charge, i.e. the pH value at which surface negative charge equals positive charge). Silica materials have very low PZC (a great tendency to lose protons) and are negatively charged over most of the pH range (Elimelech et al., 1995). As seen from Table 4-9 and Fig. 4-2, pH values of all water samples in the Aquod area are less than or just equal to the PZC of kaolinite, and are much greater than that of quartz. The pH values of water samples from the Udult area are higher than the PZC of kaolinite. Thus, based on pH and PZC data, quartz should be highly dispersed (high surface charge) in both soils, and kaolinite should be more prone to dispersion in the Udult. These theoretical tendencies are consistent with the results. Laboratory experiments also confirmed that the PZC of the colloids released from pore media matrix was the same as that of corresponding natural groundwater colloids (Ryan and Gschwend, 1990 and 1994).

Table 4-9. PZC values for common soil minerals.

Minerals	PZC	referenced
SiO ₂	2-3	Parks, 1965
Kaolinite	4.6	Stumm and Morgan, 1970
Gibbsite	5.0	Stumm and Morgan, 1970
α -Al(OH) ₃	5.0	Stumm and Morgan, 1970
α -Fe ₂ O ₃	6.7	Stumm and Morgan, 1970
Geothite	7.7	Atkinson et al., 1967
Fe(OH) ₃ amorphous	8.5	Breeuwsma, 1973
Al ₂ O ₃ amorphous	8.0	Puls et al., 1993

Dispersibility of colloids in soils of the southeastern USA is related to the amount of erodible-sized sediments (Miller and Baharuddin, 1986 and 1987). A significant proportion of total sediment collected from these soils has been found to be clay sized (< 2 μ m). Measurements of clay dispersion for a range of southeastern soils indicated that they are quite dispersive, with a median of roughly 50 % of the total clay being dispersible with vigorous shaking in water (mechanically dispersive by Emerson's classification) (Miller and Baharuddin, 1986). This observation is puzzling given that the majority of southeastern soils are kaolinitic, which theoretically requires relatively high pH for effective dispersion (Schofield and Samson, 1954). Explanations for this difference in behavior between the reference mineral and soil kaolinite have included the interaction of smectite with kaolinite edge to increase dispersibility (Arora and Coleman, 1979), and the presence of organic coatings, which increases repulsive charge (Durgin

and Chaney, 1984; Shanmuganathan and Oades, 1983). A strong correlation between soil dispersible OC and the dispersibility of soil matrices was observed in this study (Fig. 4-19) (the dispersibility was here expressed by the ratio of readily-dispersible colloids and pH10 water-dispersible colloids). The dispersibility of soil matrices, however, was not related to total soil colloid mass (Fig. 4-20). Also, TS of groundwater was not necessarily proportional to the dispersibility of corresponding soil matrix (Fig. 4-21). Thus, factors affecting the TS and colloid concentrations of in-situ groundwater are too complex to be explained by colloidal characteristics of the soil matrix from which the sample is collected. This is analogous to the sediments in a river not matching the composition of an adjacent bank, due to the entrainment and mobilization of sediments.

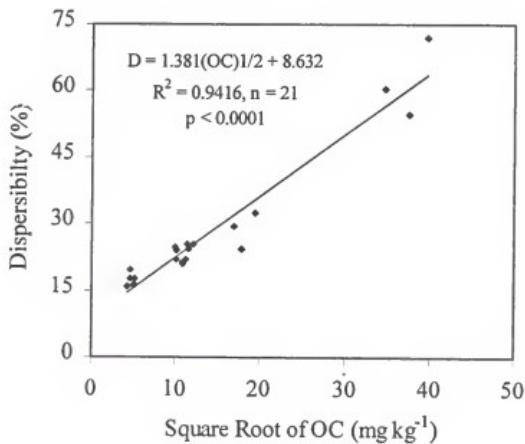


Fig. 4-19. Dispersibility of soil matrices as related to soil OC.

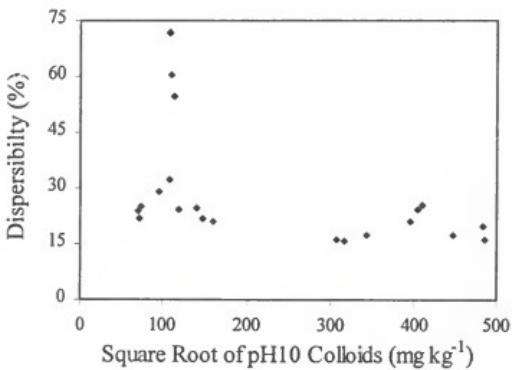


Fig. 4-20. Dispersibility of soil matrices as related to soil pH10 water-dispersible colloids ($n = 21$).

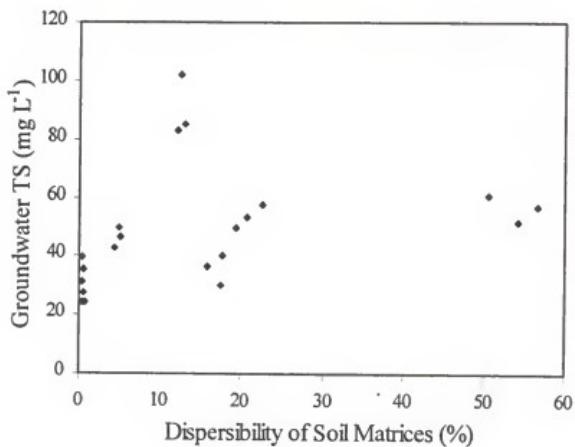


Fig. 4-21. Correlation of total solid concentration (TS) of groundwater with dispersibility of soil matrices. TS for each specific piezometer is an average of all data during sampling period ($n = 21$).

The XRD data (Table 4-8) showed higher XRD indices of RDC HIM than those of pH10 water-dispersible HIM, which suggested that HIM is more mobile. A similar finding was reported by Harris et al. (1987). However, colloidal mineralogy of actual groundwater samples did not confirm greater HIM mobility in the present study.

Colloid size and number distribution

The distribution of colloid size in natural systems is the result of dispersion mechanisms and of a number of processes which either bring the colloids together (flocculation) or disrupt existing aggregates (Filella and Buffle, 1993). The size of colloids is of fundamental importance because this parameter controls many of the general properties. Knowledge of the size distribution is also essential for understanding the processes governing both the kinetics of aggregation and the adsorption capacity. Furthermore, the importance of colloids to environmental issue is size related, due to the size dependency for surface area and reactivity. Therefore, the determination of size distribution is usually a component of colloid characterization.

Colloids occur at low concentration in groundwater and may be gravimetrically dominated by relatively large particles that nonetheless contribute little to total specific surface area. The results of dynamic light scattering analysis (Fig. 4-22) showed that even 0.1 % (by number) particles whose sizes are greater than $1 \mu\text{m}$ could constituted 50 % of total colloid volume, but contributed only 9 % to the total specific surface area. Therefore, the assessment of colloid reactivity must be based on size distribution as well as concentration.

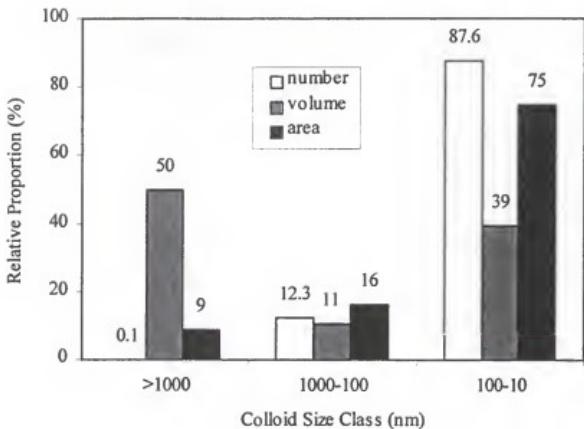


Fig. 4-22. Proportional comparisons of the number, volume (mass), and specific surface area of colloids at different size classes (a RDC sample of the Uduto-Bt horizon, analyzed using dynamic light scattering).

Results from dynamic light scattering analysis indicated that almost all of readily-dispersible colloids for both soils fall in the size range of 1.0 - 0.1 μm ($> 0.1 \mu\text{m}$), while the size distribution of groundwater colloids varies with soil and horizons (Fig. 4-23). Predominant sizes of the Aquod groundwater colloids are much smaller than those of the Uduto groundwater colloids. This, in conjunction with greater TS in the Aquod groundwater, suggested that the prevailing physico-chemical conditions in the Aquod environment are more dispersive with respect to colloids. The colloid size distribution within this range ($< 0.1 \mu\text{m}$) was also found in groundwater samples by Gschwend and Reynolds (1987), and was repeatedly observed using TEM (transmission electron

microscopy) in samples from various aquatic systems (Filella et al., 1993; Newman et al., 1994; Pizarro-Konsak et al., 1994; Rees and Ranville, 1990).

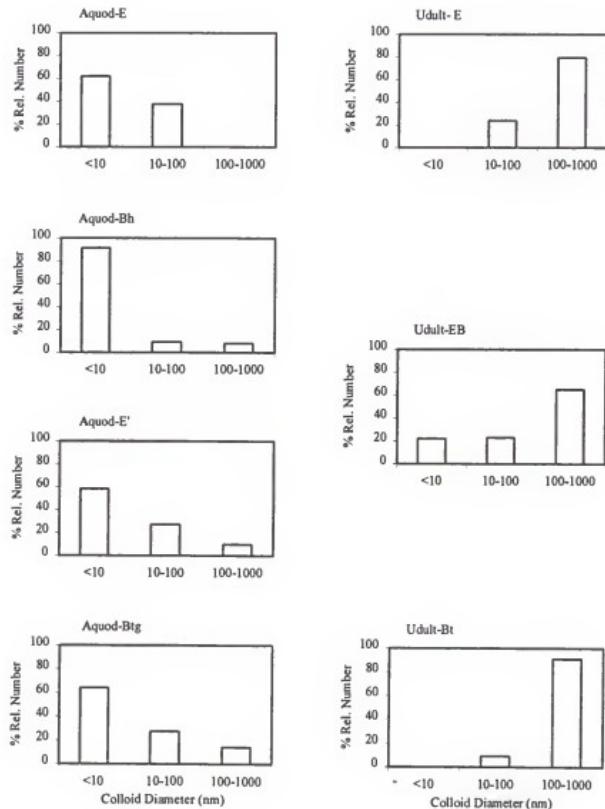


Fig. 4-23. Size distribution of groundwater colloids from corresponding horizons of Aquod and Udult, as determinated via ultrafine particle analyzer. Bars represent relative number abundances in colloid size classes.

A higher ratio of fine clay to total clay in the illuvial horizon than that in the eluvial horizon (Nettleton et al., 1987) suggests not only a greater mobility and dispersibility of the fine clay but also a possibility of flocculation and entrapment while moving through the soil matrix.

Colloids moving through a porous medium are subject to a number of interactions with the medium, which collectively are commonly referred to as *filtration*. Filtration likely occurs where pores are too small for suspended colloids to move through. Laboratory experiments have shown that colloid filtration is a major retention mechanism governing their transport through artificial porous media (Avogadro and De Marsily, 1984), but colloids are minimally trapped in geologic media (Apps et al., 1983). Therefore, dominance of finer colloids suspended in groundwater may result the selective removal of coarse colloids by filtration. Suspended colloids of comparable size to that of the pores could be trapped in the porous medium and clog the medium internally (Elimelech et al., 1995). Ultimately, the pores through which colloids can pass tend to become fewer and smaller for illuvial accumulation zones, and only ultrafine colloids continue to be entrained in groundwater. For such a case, the colloid size distribution would be related more to medium morphology than to groundwater hydrodynamics.

Organic matter adsorption on surfaces of mineral colloids promotes their dispersion, either by steric stabilization (high adsorption densities) (Tipping and Higgins, 1982) or via electrostatic effects (low adsorption densities) (Tipping and Ohnsad, 1984). Colloids ranging from $1.0 \mu\text{m}$ to $0.1 \mu\text{m}$ have been found in most natural aquatic environments and thought to be most dispersible (Filella and Buffle, 1993). However,

open aquatic systems are different from groundwater, since the former accommodate broader size ranges of colloids (usually $> 0.1 \mu\text{m}$) than the latter. Also, colloids finer than $0.1 \mu\text{m}$ might not be effectively accounted for due to the difficulty in measurements and the limitation of classical theory such as DLVO that fails to explain the existence of a relatively high concentration of colloids smaller than $0.1 \mu\text{m}$ (Filella and Buffle, 1993).

The predominant size class of RDC was $> 0.1 \mu\text{m}$, whereas the pH10 water-dispersible colloids were mainly less than $0.1 \mu\text{m}$ in size (Table 4-10). This suggests that under normal field condition, there are few mobile colloids $< 0.1 \mu\text{m}$ in size, which was not the case based on light scattering results. This discrepancy is an another example of the failure of soil matrix colloid proportions alone to predict groundwater colloid characteristics.

Table 4-10. Size distributions of soil RDC[†] and pH10 water-dispersible colloids from various horizons of the Aquod and Udult, as determined via ultrafine particle analyzer. Data in table reflect relative number abundances in colloid diameter classes.

Soil	Horizon	RDC (%)			pH10 (%)	
		$>1 \mu\text{m}$	1-0.1 μm	0.1-0.01 μm	1-0.1 μm	0.1-0.01 μm
Aquod	E	0.3	99.7	--	100.0	0.0
	Bh	0.4	99.6	--	99.9	0.1
	E'	0.5	99.5	--	92.4	7.6
	Btg	0.9	99.5	--	85.7	14.3
Udult	E	0.0	100.0	--	85.5	14.5
	EB	0.7	99.3	--	70.1	26.6
	Bt	3.8	96.2	--	99.8	0.2

† Readily-dispersible colloids.

Characteristics of Colloids as Related to Hydrodynamics

Pore water flow velocity has been reported to be directly related to colloid mobilization based on simulation experiments (McDowell-Boyer, 1992; Kaplan et al., 1993). Unfortunately, there are little field observation data available to quantitatively verify the relation between physical disturbance and the characteristics of colloids such as concentration, particle size distribution, etc. Rainfall is a main recharge source of shallow groundwater for this study site, and the infiltration of rainwater through the vadose zone is likely a significant physical disturbance. Heavy rain events could directly cause miscible displacement of ion-laden aqueous solution initially present in the soil with infiltrating low ionic rain water influent, and thereby promote the dispersion and mobilization of soil colloids. However, it is difficult to verify the relationships between rainfall rate and the extent of colloid mobilization based on field observations (Ryan and Elimelech, 1996).

Higher piezometric heads correlated weakly but significantly with higher concentrations of TS in groundwater (Fig. 4-24). A very strong predictive relationship between TS and piezometric head was not expected, because soil horizons vary in physical and chemical properties that also affect colloid mobilization as addressed in the previous section. As well, the anisotropic influence of the soil matrix (such as differential OC reductions with depth) could overshadow the role of the hydrodynamics of groundwater in colloid mobilization and greatly increase the difficulty of predicting colloid transport based on the groundwater dynamic data.

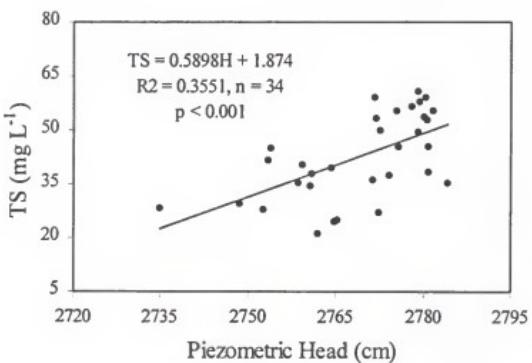


Fig. 4-24. Groundwater TS as related to piezometric head.

Summary

Some attributes of groundwater were strongly influenced by soil matrix properties of the Aquod and Udlult. Lower pH, higher EC, and higher TS and OC concentrations were persistently observed in groundwater samples from the Aquod area, where groundwater tables were always higher. Significant decreases in both TS and OC concentrations in groundwater occurred with depth for both soil areas. Colloid sizes were generally less than $1 \mu\text{m}$ in diameter, but the colloids suspended in the Aquod groundwater (dominated by $<10 \text{ nm}$ colloids) were much finer than those in the Udlult groundwater (dominated by $>100 \text{ nm}$ colloids). The spatial variability of groundwater properties and colloid characteristics (such as TS, OC, etc.) within and between the soils

was significant; variations with sampling date were greater for upper sandy zones than for deeper horizons.

Mineralogy of groundwater colloids and soil matrices colloids differed markedly. Colloids in groundwater samples from all horizons were dominated by quartz, even though argillic horizons contained a very low or undetectable proportions of colloidal quartz. This suggests that silica colloids tend to be more mobile than other components in this case. Furthermore, indicators of colloid concentrations in groundwater were not correlated with soil colloid dispersibility. The proportion of OC to TS in groundwater was higher than that in soil matrices. These results imply that colloidal materials entrained in groundwater probably originate from the surface or surrounding areas.

CHAPTER 5 CONCLUSIONS

Characteristics of groundwater colloids are basically influenced by soil morphological features and hydrological settings in the research area.

Concentrations of inorganic colloids, TS, and OC suspended in groundwater differed significantly between the two soils of the study area. Concentrations of TS and OC decreased with sampling depths for both soils. Lower pH, higher EC, and higher colloid- and OC concentrations were persistently observed in groundwater samples from the Aquod area, relative to those of the Uduto area. Groundwater colloids were generally less than 1 μm in size, but were two orders of magnitude smaller for the Aquod than the Uduto. Variation of these parameters with sampling date was insignificant.

Mineralogy of groundwater -and soil matrix colloids differed markedly. Colloids in groundwater from all horizons were dominated by quartz, even in the case of argillic horizons which contained little or no detectable quartz in the clay fraction. This suggests that silica colloids tend to be more mobile than other components for the soils and landscapes represented by the study area. There was no significant correlation between (1) colloid concentration in groundwater and soil colloid dispersibility, and (2) the proportions of OC in groundwater and that of the soil readily-dispersible fraction. Also, the proportions of organic components in total solids of groundwater were higher than those of the soil matrices. These results suggest that colloids suspended in groundwater

originate from the soil surface or surrounding areas, and in large part are not derived from the soil matrices from which the groundwater is sampled. In effect, the colloids are entrained, mobile, and capable of serving as transport vectors.

The piezometric surface controlling the watertable is dictated by the argillic horizon water pressure most of the time. Possibly, the argillic water pressure relates to watershed hydrodynamic factors, such as velocity and flow path length, which would directly influence colloid and salt entrainment. A correlation between concentration of total solid concentrations and piezometric heads suggests possible influence of hydrodynamic force on colloid mobilization. However, this relationship would be confounded by the influence of downward vertical flow of rainwater, organic matter production near the soil surface, and other physico-chemical characteristics of the soil horizons through which groundwater flows.

The following specific conclusions can be drawn:

- (1) Higher colloid- and organic C contents in groundwater generally correspond to higher piezometric head and longer water residence time.
- (2) Mineralogy of groundwater- and soil matrix colloids differ markedly. Quartz dominates the inorganic components of groundwater colloids, suggesting that silica colloids are more mobile than other components for the soils.
- (3) The proportion of organic C is higher in groundwater solids than in the readily-dispersible fraction of soil matrices.
- (4) Groundwater colloids are generally less than 1 μm in size, but size distribution seems to more relate to the soil chemical properties than physical conditions.

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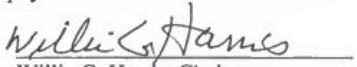
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BIOGRAPHICAL SKETCH

Zhengxi Tan was born in Jiangsu, China, on January 19, 1959. He earned a Bachelor's degree and a Master's degree with a major of Soil Science from Nanjing Agricultural University, Nanjing, China, in July 1982 and in August 1988, respectively. He, as an assistant professor, had worked in the Department of Soil Science at the same University from 1988 to 1993. In August 1993, he won the Netherlands Government Fellowship and became a research fellow in the International Institute for Aerospace Survey and Earth Sciences, Netherlands. In January of 1995, he was enrolled as a Ph.D. candidate in the Soil and Water Science Department, University of Florida. His research interests include environmental pedology, vadose zone hydrology, and GIS application. Mr. Tan received a degree of Doctor of Philosophy under the supervision of Dr. Willie G. Harris in August, 1998.

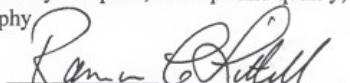
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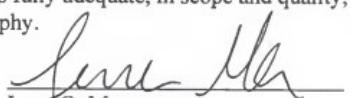
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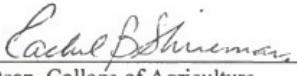

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This dissertation was submitted to the Graduate Faculty of the College of Agriculture and to the Graduate School and was accepted as partial fulfillment of the requirements for the degree of Doctor of Philosophy.

August, 1998



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